

# ***ENVIRONMENTAL CONTAMINANTS***

## ***EVALUATION***

### ***OF***

## ***ST. ANDREW BAY, FLORIDA***

### **Volume 3 Appendices**

Appendix One - Migratory Bird List

Appendix Two - Endangered Species List

Appendix Three - Standard Operating Procedures  
for  
Sediment Sampling for Chemical Analyses

Appendix Four - Standard Operating Procedures  
for  
Collection of Fish and Invertebrate Samples

Appendix Five - Laboratory Analytical Procedures

Michael S. Brim  
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U.S. Fish and Wildlife Service  
Division of Ecological Services  
Panama City Field Office  
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FEDERAL BUREAU OF INVESTIGATION  
UNITED STATES DEPARTMENT OF JUSTICE

WASH. FIELD OFFICE  
COMMUNICATIONS SECTION  
FBI - WASH. FIELD

**APPENDIX ONE**  
**MIGRATORY BIRD LIST**



Appendix 1. Bay County migratory bird list compiled from Audubon Society Christmas bird counts.

	<u>1987</u>	<u>1988</u>	<u>1989</u>	<u>1990</u>	<u>1991</u>	<u>1992</u>
Common Loon	134	107	251	255	173	286
Pied-billed Grebe	56	65	64	73	39	53
Horned Grebe	278	387	418	58	305	348
Northern Gannett	22	0	10	4	20	2
American White Pelican	0	7	0	1	0	31
Brown Pelican	348	577	528	532	224	217
Double-crested Cormorant	866	1101	2902	2308	1015	1162
Anhinga	4	5	4	9	3	2
American Bittern	0	1	0	0	0	0
Great Blue Heron	81	47	96	87	38	79
Great Blue Heron(white form)	0	0	0	1	0	0
Great Egret	44	124	51	56	49	97
Snowy Egret	42	81	37	45	58	86
Little Blue Heron	17	16	14	34	13	26
Tri-colored Heron	2	7	3	12	6	12
Reddish Egret	1	7	4	9	1	11
Green-backed Heron	3	1	1	1	1	2
Black-crowned Night Heron	2	8	6	1	1	0
Yellow-crowned Night Heron	0	0	0	0	1	0
Green-winged Teal	0	1	0	1	0	0
Wood Duck	7	9	32	10	12	20
Mallard	46	12	80	0	52	42
N. Pintail	0	0	1	0	4	1
Blue-winged Teal	4	2	0	1	0	2
Northern Shoveler	0	0	1	0	0	0
American Widgeon	2	2	1	12	4	8
Gadwall	0	0	42	6	0	0
Canvasback	2	0	0	0	0	0
Redhead	407	844	388	26	379	27
Ring-necked Duck	222	22	26	21	43	77
Greater Scaup	0	5	9	0	0	0
Lesser Scaup	19	145	129	38	137	596
Scaup, spp.	24	36	1	0	0	0
Oldsquaw	1	0	0	0	0	0
Common Goldeneye	68	70	36	109	86	40
Bufflehead	123	426	428	529	329	335
Hooded Merganser	98	59	36	57	100	42

Appendix 1 cont'd. Bay County migratory bird list compiled from Audubon Society Christmas bird counts.

	<u>1987</u>	<u>1988</u>	<u>1989</u>	<u>1990</u>	<u>1991</u>	<u>1992</u>
Red-breasted Merganser	241	443	585	396	303	274
Ruddy Duck	4	2	30	4	2	0
Black vulture	0	0	1	6	1	2
Turkey vulture	6	5	31	6	1	42
Osprey	7	5	6	14	5	19
Bald Eagle*	1	0	0	0	0	3
Northern Harrier	2	8	1	1	0	2
Sharp-shinned Hawk	1	3	3	4	2	5
Cooper's Hawk	0	1	1	3	2	2
<i>Accipiter, sp.</i>	0	1	0	0	0	0
Red-shouldered Hawk	2	1	0	7	3	7
Red-tailed Hawk	10	11	7	8	11	13
American Kestrel	16	21	20	27	28	33
Merlin	0	0	1	0	0	1
Peregrin Falcon*	0	1	0	0	0	0
Northern Bobwhite	1	7	2	3	0	0
Clapper Rail	7	3	2	5	8	3
King Rail	0	1	2	0	0	0
Sora	2	2	5	2	3	2
Virginia Rail	3	4	1	3	1	0
Purple Gallinule	0	2	0	0	0	0
Common Moorhen	52	75	80	58	56	50
American Coot	309	101	149	116	160	264
Black-bellied Plover	51	109	67	103	84	44
Snowy Plover***	24	15	30	17	33	5
Semipalmated Plover	25	41	35	117	72	8
Piping Plover**	4	0	29	9	17	91
Killdeer	74	94	473	115	162	135
Greater Yellowlegs	11	8	4	7	6	22
Lesser Yellowlegs	0	2	2	0	3	0
Willet	48	94	95	105	94	105
Spotted Sandpiper	5	3	4	6	6	3
Whimbrel	1	0	1	2	0	1
Marbled Godwit	3	0	2	4	0	1
Ruddy Turnstone	56	188	75	95	86	78

Appendix 1 cont'd. Bay County migratory bird list compiled from Audubon Society Christmas bird counts.

	<u>1987</u>	<u>1988</u>	<u>1989</u>	<u>1990</u>	<u>1991</u>	<u>1992</u>
Red Knot	0	242	36	0	1	0
Sanderling	154	265	281	195	241	170
Western Sandpiper	2	35	19	76	8	1
Least Sandpiper	14	8	16	22	12	1
Dunlin	326	766	409	185	278	94
peep spp.	0	40	0	0	0	0
Short-billed Dowitcher	2	87	168	30	26	137
Common Snipe	8	4	19	8	5	5
American Woodcock	2	2	4	1	3	2
Wilson's Phalarope	0	0	1	0	0	0
Laughing Gull	643	1002	932	1373	941	1219
Bonaparte's Gull	274	95	898	1041	592	371
Ring-billed Gull	697	822	1150	738	537	729
Herring Gull	200	279	250	198	139	137
Black-legged Kittiwake	0	0	0	1	0	0
Caspian Tern	0	9	1	0	0	0
Royal Tern	123	81	165	133	112	79
Sandwich Tern	1	1	0	1	5	0
Forster's Tern	81	102	166	275	62	134
Black Skimmer	9	85	106	67	3	81
Rock Dove	227	247	75	212	345	35
Mourning Dove	574	606	679	1690	1691	1258
Common Ground Dove	25	5	10	2	11	7
Budgerigar	0	0	0	1	0	0
Barn Owl	0	0	0	1	1	0
Eastern Screech Owl	1	3	2	1	4	3
<i>Selaphorus sp.</i>	0	0	0	0	1	0
Black-chinned Hummingbird	0	1	0	0	1	0
Rufous Hummingbird	0	0	0	0	1	0
Barred Owl	0	0	1	2	3	0
Ruby-throated Hummingbird	0	0	0	1	0	0
Belted Kingfisher	50	53	49	63	57	67
Red-headed Woodpecker	2	0	1	0	0	1
Red-bellied Woodpecker	28	23	43	49	39	43
Yellow-bellied Sapsucker	2	3	12	12	8	4
Downy Woodpecker	3	13	10	5	5	10

Appendix 1 cont'd. Bay County migratory bird list compiled from Audubon Society Christmas bird counts.

	<u>1987</u>	<u>1988</u>	<u>1989</u>	<u>1990</u>	<u>1991</u>	<u>1992</u>
Northern Flicker	26	10	17	54	48	35
Pileated Woodpecker	2	0	2	0	0	3
Eastern Phoebe	1	8	21	28	31	34
Tree Swallow	154	334	188	39	86	41
Blue Jay	103	145	242	571	327	363
American Crow	1	3	1	0	1	2
Fish Crow	261	108	112	70	22	60
Carolina Chickadee	38	51	22	26	29	53
Tufted Titmouse	13	17	25	30	28	22
Redbreasted Nuthatch	0	1	14	0	0	0
Brownheaded Nuthatch	17	28	34	27	10	109
Brown Creeper	0	0	1	1	0	0
Carolina Wren	19	44	67	100	65	75
House Wren	7	18	33	16	4	10
Winter Wren	0	1	0	0	0	0
Sedge Wren	3	2	6	3	3	1
Marsh Wren	2	11	12	9	9	5
Golden-crowned Kinglet	0	5	0	2	0	0
Ruby-crowned Kinglet	42	133	92	104	108	117
Blue-gray Gnatcatcher	7	15	19	13	14	18
Eastern Bluebird	2	12	5	57	15	34
Hermit Thrush	1	3	8	5	10	1
American Robin	1869	31	3545	5536	354	1120
Varied Thrush	0	1	0	0	0	0
Gray Catbird	12	27	42	45	34	13
Northern Mockingbird	84	83	280	260	168	162
Brown Thrasher	8	6	6	29	20	4
Cedar Waxwing	124	20	1400	100	14	44
Loggerhead Shrike	20	20	9	13	14	28
European Starling	1632	1743	1279	1818	3024	1234
White-eyed Vireo	0	1	7	2	3	0
Solitary Vireo	3	5	4	9	5	6
Orange-crowned Warbler	0	2	2	18	3	5
Yellow-rumped Warbler	855	1424	2441	2548	1367	2194
Yellow-throated Warbler	6	7	1	4	4	4
Pine Warbler	43	125	56	182	64	56

Appendix 1 cont'd. Bay County migratory bird list compiled from Audubon Society Christmas bird counts.

	<u>1987</u>	<u>1988</u>	<u>1989</u>	<u>1990</u>	<u>1991</u>	<u>1992</u>
Palm Warbler	0	4	1	0	1	3
Black-and-white Warbler	0	1	2	0	1	1
<i>Oporornis, sp.</i>	0	1	0	0	0	0
Common Yellowthroat	3	20	20	14	15	17
W. Tanager	0	0	0	0	1	0
Northern Cardinal	46	75	124	184	116	130
Rufous-sided Towhee	72	46	106	108	71	36
Chipping Sparrow	115	84	88	299	29	34
Field Sparrow	9	27	11	0	3	1
Vesper Sparrow	1	1	2	0	0	0
Savannah Sparrow	13	40	58	201	9	69
Le Conte's Sparrow	0	0	1	0	0	0
Sharp-tailed Sparrow	8	13	8	4	17	19
Seaside Sparrow	4	15	2	3	11	0
Song Sparrow	30	41	87	70	30	42
Lincoln's Sparrow	0	1	0	0	0	0
Swamp Sparrow	31	58	17	39	26	24
White-throated Sparrow	48	15	74	66	26	14
White-crowned Sparrow	0	1	0	0	0	2
Dark-eyed Junco	0	0	20	0	0	0
Red-winged Blackbird	79	503	328	275	788	84
Eastern Meadowlark	57	11	145	15	61	61
Rusty Blackbird	0	100	0	0	0	0
Brewer's Blackbird	0	40	0	0	0	0
Boat-tailed Grackle	0	0	0	0	1506	0
Common Grackle	10	427	1447	1005	0	329
Brown-headed Cowbird	6	1107	37	567	8	214
House Finch	0	0	0	0	0	1
Purple Finch	5	4	3	7	1	0
American Goldfinch	111	49	205	130	31	255
House Sparrow	124	95	151	281	144	227
<i>Number of Species</i>	127	142	144	131	130	127
<i>Total No. of Individuals</i>	12443	17529	25872	27007	18152	16884

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**APPENDIX TWO**  
**ENDANGERED SPECIES LIST**



THREATENED, ENDANGERED, AND OTHER SPECIAL-STATUS SPECIES LIKELY TO OCCUR IN BAY COUNTY, FL  
Compiled by U.S. Fish and Wildlife Service, April 1998

Common Name	Scientific Name	Status State	Status FWS	Natural Communities
<b>FISH:</b>				
Gulf sturgeon	<i>Acipenser oxyrinchus desotoi</i>	SSC	T	ESTUARINE: various MARINE: various habitats RIVERINE: alluvial and blackwater streams
Shoal bass	<i>Micropterus sp. (undescribed)</i>	SSC		RIVERINE: alluvial stream
Bluenose shiner	<i>Pteronotropsis welaka</i>	SSC		RIVERINE: blackwater, alluvial, and spring-run streams
<b>AMPHIBIANS &amp; REPTILES:</b>				
American alligator	<i>Alligator mississippiensis</i>	SSC	T(s/a)	ESTUARINE: marshes, various habitats LACUSTRINE: marshes, swamps, various habitats PALUSTRINE: swamps, floodplains, marshes, various habitats RIVERINE: open water, shorelines, various habitats
Loggerhead turtle	<i>Caretta caretta</i>	T	T	ESTUARINE: submersed vegetation, hard bottoms, open water, various MARINE: open water, hard bottoms, various TERRESTRIAL: beach dune-nesting
Green turtle	<i>Chelonia mydas mydas</i>	E	E	ESTUARINE: submersed vegetation, hard bottoms, open water, various MARINE: open water, hard bottoms TERRESTRIAL: beach dune-nesting
Leatherback turtle	<i>Dermochelys coriacea</i>	E	E	ESTUARINE: submersed vegetation, hard bottoms, open water, various MARINE: open water, hard bottoms TERRESTRIAL: beach dune-nesting
Eastern indigo snake	<i>Drymarchon corais couperi</i>	T	T	ESTUARINE: tidal swamp PALUSTRINE: hydric hammock, wet flatwoods TERRESTRIAL: mesic flatwoods, upland pine forest, sandhills, scrub, scrubby flatwoods, rockland hammock, ruderal
Hawksbill turtle	<i>Eretmochelys imbricata imbricata</i>	E	E	MARINE: open water
Gopher tortoise	<i>Gopherus polyphemus</i>	SSC	ce	TERRESTRIAL: sandhills, scrub, scrubby flatwoods, xeric hammocks, coastal strand, ruderal
Atlantic ridley turtle	<i>Lepidochelys kempi</i>	E	E	ESTUARINE: open water MARINE: open water

THREATENED, ENDANGERED, AND OTHER SPECIAL-STATUS SPECIES LIKELY TO OCCUR IN BAY COUNTY, FL  
Compiled by U.S. Fish and Wildlife Service, April 1998

Common Name	Scientific Name	Status State	Status FWS	Natural Communities
Alligator snapping turtle	<i>Macrocllemys temminckii</i>	SSC	ce	ESTUARINE: tidal marsh LACUSTRINE: river floodplain lake, swamp lake RIVERINE: alluvial stream, blackwater stream
Gulf salt marsh snake	<i>Nerodia clarkii clarkii</i>		ce	ESTUARINE: tidal marsh, tidal swamp MARINE: tidal marsh, tidal swamp
Florida pine snake	<i>Pituophis melanoleucus mugitus</i>	SSC	ce	LACUSTRINE: ruderal, sandhill upland lake TERRESTRIAL: sandhill, scrubby flatwoods, xeric hammock, ruderal
Gopher frog	<i>Rana capito</i>	SSC	ce	TERRESTRIAL: sandhill, scrub, scrubby flatwoods, xeric hammock (reproduces in ephemeral wetlands within these communities)
<b>BIRDS:</b>				
Bachman's sparrow	<i>Aimophila aestivalis</i>		ce	TERRESTRIAL: various, ruderal
Southeastern snowy plover	<i>Charadrius alexandrinus tenuirostris</i>	T	ce	ESTUARINE: exposed unconsolidated substrate MARINE: exposed unconsolidated substrate TERRESTRIAL: beach dune
Piping plover	<i>Charadrius melodus</i>	T	T	ESTUARINE: exposed unconsolidated substrate (wintering migrant) MARINE: exposed unconsolidated substrate TERRESTRIAL: beach dune
Marian's marsh wren	<i>Cistothorus palustris marianae</i>	SSC		ESTUARINE: tidal marsh MARINE: tidal marsh
Stoddard's yellow-throated warbler	<i>Dendroica dominica stoddardi</i>		ce	TERRESTRIAL: wooded habitats with spanish moss, various
Little blue heron	<i>Egretta caerulea</i>	SSC		ESTUARINE: marshes, shoreline PALUSTRINE: floodplains, swamps RIVERINE: shoreline
Snowy egret	<i>Egretta thula</i>	SSC		ESTUARINE: marshes, tidal swamps, shoreline LACUSTRINE: lake edges PALUSTRINE: swamp, floodplain, ruderal RIVERINE: shoreline
Tricolored heron	<i>Egretta tricolor</i>	SSC		ESTUARINE: marshes, tidal swamps, shoreline LACUSTRINE: lake edges PALUSTRINE: swamp, floodplain, ruderal RIVERINE: shoreline

THREATENED, ENDANGERED, AND OTHER SPECIAL-STATUS SPECIES LIKELY TO OCCUR IN BAY COUNTY, FL  
Compiled by U.S. Fish and Wildlife Service, April 1998

Common Name	Scientific Name	Status State	Status FWS	Natural Communities
Arctic peregrine falcon	<i>Falco peregrinus tundrius</i>	E	E(s/a)	ESTUARINE: winters along coasts LACUSTRINE: various PALUSTRINE: various TERRESTRIAL: various, ruderal
Southeastern kestrel	<i>Falco sparverius paulus</i>	T	ce	ESTUARINE: various habitats PALUSTRINE: various habitats TERRESTRIAL: open pine forests, clearings, ruderal, various
Bald eagle	<i>Haliaeetus leucocephalus</i>	T	T	ESTUARINE: marsh edges, tidal swamp, open water LACUSTRINE: swamp lakes, edges PALUSTRINE: swamp, floodplain RIVERINE: shoreline, open water TERRESTRIAL: pine and hardwood forests, clearings
Wood stork	<i>Mycteria americana</i>	E	E	ESTUARINE: marshes LACUSTRINE: floodplain lakes, marshes (feeding), various PALUSTRINE: marshes, swamps, various
Brown pelican	<i>Pelecanus occidentalis</i>	SSC		ESTUARINE: islands for nesting, open water MARINE: open water
Red-cockaded woodpecker	<i>Picoides borealis</i>	T	E	TERRESTRIAL: mature longleaf, slash, and loblolly pine forests
Least tern	<i>Sterna antillarum</i>	T		ESTUARINE: various LACUSTRINE: various RIVERINE: various TERRESTRIAL: beach dune, ruderal
<b>MAMMALS:</b>				
Choctawhatchee beach mouse	<i>Peromyscus polionotus allopnyrs</i>	E	E	TERRESTRIAL: beach dune, coastal grassland
St. Andrew beach mouse	<i>Peromyscus polionotus peninsularis</i>	E	PE	TERRESTRIAL: beach dune, coastal grassland
West Indian manatee	<i>Trichechus manatus latirostris</i>	E	E	ESTUARINE: submerged vegetation, open water MARINE: open water, submerged vegetation RIVERINE: alluvial stream, blackwater stream, spring-run stream
Florida black bear	<i>Ursus americanus floridanus</i>	T	C	PALUSTRINE: titi swamps, floodplains TERRESTRIAL: pine and hardwood forests
<b>INVERTEBRATES:</b>				
Gulf moccasinshell	<i>Medionidus penicillatus</i>		E	RIVERINE: medium-sized creeks to large rivers with sand and gravel substrates in slow to moderate currents
<b>PLANTS:</b>				

Common Name	Scientific Name	Status State	Status FWS	Natural Communities
Southern milkweed	<i>Asclepias viridula</i>	T	ce	PALUSTRINE: wet prairie, seepage slope edges RIVERINE: seepage stream banks TERRESTRIAL: mesic flatwoods, drainage ditches
Pine-woods aster	<i>Aster spinulosus</i>	E	ce	PALUSTRINE: seepage slope TERRESTRIAL: sandhill, scrubby and mesic flatwoods
Apalachicola wild indigo	<i>Baptisia megacarpa</i>	E		PALUSTRINE: floodplain forest TERRESTRIAL: upland mixed forest, slope forest
Toothed savory	<i>Calamintha dentata</i>		ce	TERRESTRIAL: sandhill, roadsides
Curtiss' sandgrass	<i>Calamovilfa curtissii</i>	T	ce	PALUSTRINE: mesic and wet flatwoods, wet prairie, depression marsh TERRESTRIAL: mesic flatwoods
Sweet shrub	<i>Calycanthus floridus</i>	E		TERRESTRIAL: upland hardwood forest, slope forest, bluffs PALUSTRINE: bottomland forest, stream banks, floodplains
Baltzell's sedge	<i>Carex baltzellii</i>	T	ce	TERRESTRIAL: slope forest, moist sandy loam; moist sandy loam
Godfrey's golden aster	<i>Chrysopsis godfreyi</i>		ce	TERRESTRIAL: beach dunes, coastal grassland
Cruise's golden-aster	<i>Chrysopsis gossypina cruiseana</i>	E	ce	TERRESTRIAL: coastal dunes, coastal strand, coastal grassland; openings and blowouts
Rosebud orchid or spreading pagonia	<i>Cleistes divaricata</i>	T		PALUSTRINE: wet flatwoods
Alternate-leaf or pagoda dogwood	<i>Cornus alternifolia</i>	E		PALUSTRINE: creek swamps TERRESTRIAL: slope forest, upland hardwood forest, bluffs
Dew-thread	<i>Drosera filifolia</i>	E		LACUSTRINE: exposed lake bottoms
Spoon-leaved sundew	<i>Drosera intermedia</i>	T		LACUSTRINE: sinkhole lake edges PALUSTRINE: seepage slope, wet flatwoods, depression marsh RIVERINE: seepage stream banks, drainage ditches
Telephus spurge	<i>Euphorbia telephioides</i>	E	T	TERRESTRIAL: mesic flatwoods; disturbed wiregrass ( <i>Aristida stricta</i> ) areas
Wiregrass gentian	<i>Gentiana pennelliana</i>	E	ce	PALUSTRINE: seepage slope, wet prairie, roadside ditches TERRESTRIAL: mesic flatwoods, planted slash pine
Mock pennyroyal	<i>Hedeoma graveolens</i>		ce	TERRESTRIAL: mesic flatwoods, sandhill, scrubby flatwoods, scrub forests

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E = Endangered, T = Threatened, P = Proposed, C = Candidate, s/a = Similarity of appearance

SSC = Species of Special Concern, ce = Consideration encouraged

THREATENED, ENDANGERED, AND OTHER SPECIAL-STATUS SPECIES LIKELY TO OCCUR IN BAY COUNTY, FL

Compiled by U.S. Fish and Wildlife Service, April 1998

Common Name	Scientific Name	Status State	Status FWS	Natural Communities
Panhandle spiderlily	<i>Hymenocallis henryae</i>	E	ce	PALUSTRINE: dome swamp edges, wet prairie, wet flatwoods, baygall edges, swamp edges TERRESTRIAL: wet prairies and flatwoods
Smooth-barked St. John's wort	<i>Hypericum lissophloeus</i>	E	ce	LACUSTRINE: sandhill upland lake margins TERRESTRIAL: sandhill upland lake margins
Florida anise	<i>Illicium floridanum</i>	T		PALUSTRINE: floodplain forest, baygall RIVERINE: seepage stream bank TERRESTRIAL: slope forest, seepage slope
Mountain laurel	<i>Kalmia latifolia</i>	T		RIVERINE: seepage stream bank TERRESTRIAL: slope forest, seepage stream banks
Bog-button	<i>Lachnocaulon digynum</i>		ce	PALUSTRINE: seepage slope, wet flatwoods, bog TERRESTRIAL: seepage slopes, wet flatwoods; exposed sands
Southern red lily	<i>Lilium catesbaei</i>	T		PALUSTRINE: wet prairie, wet flatwoods, seepage slope TERRESTRIAL: mesic flatwoods, seepage slope; usually with grasses
Gulf coast lupine	<i>Lupinus westianus</i>	T	ce	TERRESTRIAL: beach dune, scrub, disturbed areas, roadsides, blowouts in dunes
Curtiss' loosestrife	<i>Lythrum curtissii</i>	E	ce	PALUSTRINE: wet flatwoods edges, floodplain swamp, seepage slope, dome swamp edges TERRESTRIAL: seepage slope
White birds-in-a-nest	<i>Macbridea alba</i>	E	T	PALUSTRINE: seepage slope TERRESTRIAL: mesic flatwoods
Hummingbird flower	<i>Macranthera flammea</i>	E		PALUSTRINE: seepage slope, dome swamp edges, floodplain swamps RIVERINE: seepage stream banks TERRESTRIAL: seepage slopes
Ashe's magnolia	<i>Magnolia ashei</i>	E		TERRESTRIAL: slope and upland hardwood forest, ravines
Pyramid magnolia	<i>Magnolia pyramidata</i>	E		TERRESTRIAL: slope forest
Piedmont water-milfoil	<i>Myriophyllum laxum</i>		ce	LACUSTRINE: sandhill upland lake, submersed PALUSTRINE: floodplain and dome swamp RIVERINE: blackwater stream, roadside ditches
Giant water-dropwort	<i>Oxypolis filiformis greenmanii</i>	E		PALUSTRINE: dome swamp, wet flatwoods, ditches; in water
Papery whitlow-wort	<i>Paronychia chartacea</i>	E	T	TERRESTRIAL: Karst sandhill lake margins

T&e12.xls

Printed 4/1/98 10:58 AM

E = Endangered, T = Threatened, P = Proposed, C = Candidate, s/a = Similarity of appearance

SSC = Species of Special Concern, ce = Consideration encouraged

Common Name	Scientific Name	Status State	Status FWS	Natural Communities
Hairy fever tree	<i>Pinckneya bracteata</i>	T		PALUSTRINE: creek swamps, titi swamps, bogs
Godfrey's (violet) butterwort	<i>Pinguicula ionantha</i>	E	T	PALUSTRINE: wet flatwoods, wet prairie, bog; in shallow water RIVERINE: seepage slope; in shallow water
Yellow butterwort	<i>Pinguicula lutea</i>	T		PALUSTRINE: flatwoods, bogs
Chapman's butterwort	<i>Pinguicula planifolia</i>	T	ce	PALUSTRINE: wet flatwoods, seepage slopes, bog, dome swamp, ditches; in water
Primrose-flower butterwort	<i>Pinguicula primulifolia</i>	E		PALUSTRINE: bogs, pond margins, margins of spring runs
Bent golden aster	<i>Pityopsis flexuosa</i>	E	ce	TERRESTRIAL: sandhill, upland pine forest, ruderal
Yellow fringed orchid	<i>Platanthera ciliaris</i>	T		PALUSTRINE: bogs, wet flatwoods TERRESTRIAL: Bluff
Yellow fringeless orchid	<i>Platanthera integra</i>	E	ce	PALUSTRINE: wet prairie, seepage slope TERRESTRIAL: mesic flatwoods
Snowy orchid	<i>Platanthera nivea</i>	T		PALUSTRINE: bogs
Large-leaved jointweed	<i>Polygonella macrophylla</i>	T	ce	TERRESTRIAL: scrub, sand pine/oak scrub ridges
Meadowbeauty	<i>Rhexia parviflora</i>	E	ce	PALUSTRINE: dome swamp margin, seepage slope, depression marsh; on slopes; with hypericum
Panhandle meadowbeauty	<i>Rhexia salicifolia</i>		ce	LACUSTRINE: sandhill upland lake, shallow water
St. John's-susan	<i>Rudbeckia nitida</i>	E	ce	PALUSTRINE: wet flatwoods and prairies, roadside ditches
White-top pitcher plant	<i>Sarracenia leucophylla</i>	E	ce	PALUSTRINE: wet prairie, seepage slope, baygall edges, ditches
Parrot pitcher plant	<i>Sarracenia psittacina</i>	T		PALUSTRINE: wet flatwoods, wet prairie, seepage slope
Decumbant pitcher plant	<i>Sarracenia purpurea</i>	T		PALUSTRINE: Bogs
Florida skullcap	<i>Scutellaria floridana</i>	E	T	PALUSTRINE: seepage slope, wet flatwoods, grassy openings TERRESTRIAL: mesic flatwoods
Lace-lip	<i>Spiranthes laciniata</i>	T		PALUSTRINE: wet flatwoods

THREATENED, ENDANGERED, AND OTHER SPECIAL-STATUS SPECIES LIKELY TO OCCUR IN BAY COUNTY, FL

Compiled by U.S. Fish and Wildlife Service, April 1998

Common Name	Scientific Name	Status State	Status FWS	Natural Communities
Silky camellia	<i>Stewartia malacodendron</i>	E		PALUSTRINE: baygall PALUSTRINE: slope forest, upland mixed forest, TERRESTRIAL: slope forest, upland mixed forest; acid soils
Chapman's crownbeard	<i>Verbesina chapmanii</i>	T	ce	PALUSTRINE: seepage slope TERRESTRIAL: mesic flatwoods with wiregrass (Aristida stricta)
Drummond's yellow-eyed grass	<i>Xyris drummondii</i>		ce	PALUSTRINE: wet flatwoods, bog, seepage slopes, ditches
Quillwort yellow-eyed grass	<i>Xyris isoetifolia</i>		ce	LACUSTRINE: sandhill upland lake margins
Karst pond xyris	<i>Xyris longisepala</i>	E		PALUSTRINE: wet flatwoods, wet prairie
Harper's yellow-eyed grass	<i>Xyris scabrifolia</i>	T	ce	LACUSTRINE: sandhill upland lake margins
				PALUSTRINE: seepage slope, wet prairie, bogs

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**APPENDIX THREE**

**STANDARD OPERATING PROCEDURES**

**FOR**

**SEDIMENT SAMPLING**

**FOR**

**CHEMICAL ANALYSES**



## **STANDARD OPERATING PROCEDURES**

### **SEDIMENT SAMPLING FOR CHEMICAL ANALYSES**

To maintain and assure quality control, sediment samples collected for shipment to USFWS-approved analytical laboratories will be obtained and handled as follows:

#### **COLLECTION OF SAMPLES FROM COASTAL WATERS OR LARGE RIVERS**

1. **Sampling Devices** - The following devices are approved for obtaining sediment samples:
  - a) Ponar grab, Standard. Manufactured from 316 stainless steel including jaws, side plates, underlip plate, screen frame, screens and hinge pin. 583 micron mesh top screens; weight empty - 21 kg (45 lbs); sampling area 22.85 cm x 22.85 cm (9" x 9").
  - b) Ponar grab, Petite. Manufactured with 316 stainless steel including jaws, side plates, underlip plate, screen frame, screens and hinge pin. 583 micron mesh top screens; weight empty - 6.8 kg (15 lbs); sampling area 15.24 x 15.24 cm (6" x 6").
2. **Sediment Sampling Boat** -
  - A) fiberglass boat with outboard motor equipped as follows:
    - 1) navigation and positioning capabilities including: a) loran navigation system, b) chart-printing depth recorder, c) compass, d) appropriate navigation charts.
    - 2) 12 volt electric winch; steel ginpole with heavy duty pulley; 100' of 1/2" braided nylon lift rope.
    - 3) stainless steel wash deck equipped with an overboard wash pump.

### 3. Other Equipment and Supplies -

- A) Stainless steel sample pan 28 x 48 x 10 cm.
- B) Pre-cleaned, chemical-free, glass 1.0 liter sample jars with screw-top lids having teflon liners.
- C) Pre-cleaned, chemical-free stainless steel utensils.
- D) Clean insulated ice chests with ice.
- E) Permanent, glass-adhesive markers.
- F) Bound collection log-book or individual record sheets.
- G) Disposable laboratory gloves.
- F) Meters: dissolved oxygen, salinity, temperature, pH and others, as appropriate.

### 4. Operational Procedures -

- 1) Prior to each *collection day* the ponar sampler will be scrubbed and washed with a detergent solution, rinsed thoroughly with tap water, and then rinsed with distilled water. After each collection *field trip* the ponar will be cleaned, as above, and stored properly.
- 2) The daily collection plan shall provide, to the greatest extent possible, for sampling to begin at the least contaminated station, with work advancing toward the most contaminated station.
- 3) Sediment samples obtained at *sampling stations* will be composite samples. Each composite will consist of five individual ponar sub-samples collected 3 meters apart along a straight-line transect, with the collection boat anchored. Move from one *sub-sample position* to the next by slipping the anchor line to provide approximately 3 meters of horizontal drift.
- 4) Place each ponar sub-sample in the sample pan. Take approximately 150 grams of sediment from the center of the sub-sample using appropriate utensils and place it in the collection jar designated for that station. After obtaining each sub-sample, rinse utensils, wash deck, sample pan, and the ponar sampler with seawater or river water.

Note: 150 grams of sub-sample collected from each of the 5 sub-sample positions (about 750 grams of sample total) should result in the sample jar being about 3/4 full. This leaves adequate space in the jar for any expansion of the sample during freezing.

- 5) During collection of the third ponar sub-sample, record the *station location* by loran positions and by latitude and longitude. At this time, also record all other station information (such as depth, salinity, water temperature, etc).
- 6) Place each sub-sample (total, n=5) in the appropriate pre-labeled, sample jar. Secure the lid and place sample on ice in a cooler.
- 7) After work at each *sampling station* is complete, clean the ponar, sample pan, wash deck and utensils thoroughly and rinse with seawater or river water.
- 8) For field trips involving more than one day, samples will be frozen and stored in a portable *field freezer*.
- 9) After each collection day, double-wrap each full sample jar with clean, heavy-duty aluminum foil, place a second identification label over the foil, and store in a freezer.
- 10) Upon returning to the Panama City Field Office samples will be transferred to a *laboratory freezer* and held at -23<sup>0</sup> degrees centigrade (-10 fahrenheit) until shipment for chemical analyses. Sediment samples for particle size analysis will be held at 4<sup>0</sup> degrees C.



**APPENDIX FOUR**

**STANDARD OPERATING PROCEDURES**

**FOR**

**COLLECTION OF FISH OR INVERTEBRATE**

**TISSUE SAMPLES**



## STANDARD OPERATING PROCEDURES

### COLLECTION OF FISH OR INVERTEBRATE

#### TISSUE SAMPLES

Fish or invertebrates collected for chemical contaminant evaluations may be taken by electrofishing gear, monofilament gillnets, otter trawl, mechanical drags, haul or beach seines, fish or crab traps, trotlines, rod and reel, and SCUBA diving or snorkling. However, any collecting gear should be free of chemical treatments and/or metals that could contaminate samples. Inspect and clean any collection gear, as appropriate, prior to any collection of samples. This is particularly important when the entire fish or invertebrate will be used (whole body analysis).

For species of special concern such as Gulf sturgeon or large broodstock striped bass, we utilize only incidental mortalities, and these should be fresh specimens.

The following is a sample dissection.

1. Wash hands thoroughly and rinse completely. Wear new vinyl or latex gloves. Final rinse gloves with distilled water.
2. Fish or invertebrates should be clean. They may be rinsed of debris or mud in the waters of the collection site.
3. The dissection surface (work area) should be a chemically-inert substance such as a thoroughly washed, acetone-cleaned, and then distilled water-rinsed stainless steel pan, or counter. Avoid letting the dissected sample touch this surface, if possible.
4. Use previously cleaned, and acetone rinsed, then distilled water-rinsed stainless steel dissection tools (knives, scalpels, etc.). Scales for total fish weights and sample weights should also be clean or covered with pre-cleaned aluminum foil. Measuring devices for fish lengths, etc., should be clean, and if possible, should not come in contact with the specimen.
5. Do not let dissected samples remain exposed to the air. Exposure can dry samples and reduce the natural percentage of moisture. Prepare each dissected sample for shipping or freezing as it is dissected.

continued on following page

6. Samples should be placed in the smallest, pre-cleaned glass jar that will adequately hold the sample. The jars should be pre-labeled with a permanent, waterproof marking pen on the outside of the jar. Jars should also have a teflon liner inside the lid. As an alternative, acetone-rinsed, heavy-duty aluminum foil may be used to wrap the sample. After double-wrapping, place the sample (with sample identification label) inside an air-tight zip-lock bag.
7. Sample identification labels should be prepared with permanent, waterproof ink or other writing instruments that will not bleed out or wash out, and should provide the following information:
  - a. species name and common name,
  - b. type of tissue (if not whole body),
  - c. collection location,
  - d. latitude and longitude,
  - e. county and state,
  - f. weight of sample in grams,
  - g. date of collection,
  - h. sample collector's name,
  - i. total weight of specimen (grams),
  - j. total length, fork length or other appropriate measurements of specimen (cm), and
  - k. method of collection.
8. Samples should be frozen as soon as possible at -23° centigrade (-10° fahrenheit). If samples contain large amounts of liquids that may expand, the lids may be set on the jars, without securing, until the sample has expanded and frozen. Then lids should be secured tightly.
9. Quality 35 mm color photographs of the specimens are desirable, as well as a written description of any external or internal lesions, tumors, etc.

**APPENDIX FIVE**

**LABORATORY ANALYTICAL PROCEDURES**

**AND**

**QUALITY ASSURANCE REPORTS**



Patuxent Analytical Control Facility

U.S. Fish and Wildlife Service

Laurel, Maryland

Quality Assurance Reports



SEP - 7 1989

U. S. FISH AND WILDLIFE SERVICE  
PATUXENT ANALYTICAL CONTROL FACILITY

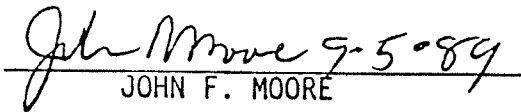
QUALITY ASSURANCE REPORT

RE:# 5652      REGION : 4      REGIONAL ID 88-4-041

THE ANALYSES ON THE ABOVE MENTIONED SAMPLES WERE PERFORMED AT:

THE MISSISSIPPI STATE CHEMICAL LABORATORY  
BOX CR  
MISSISSIPPI STATE, MISSISSIPPI 39762

THIS LABORATORY WAS SUBJECTED TO A RIGOROUS EVALUATION PROCESS PRIOR TO THE AWARDED OF IT'S CONTRACT. A PANEL OF FISH AND WILDLIFE SERVICE SCIENTISTS CERTIFIED IT TO BE TECHNICALLY QUALIFIED TO PERFORM THE ANALYSES REPORTED HERE. IN ADDITION WE HAVE CONTINUED TO CLOSELY MONITOR THIS LABORATORY'S PERFORMANCE AND HAVE FOUND THE PRECISION AND ACCURACY OF THEIR WORK REMAINS ACCEPTABLE. WE HAVE GREAT CONFIDENCE IN THE ACCURACY OF THESE DATA.

  
JOHN F. MOORE

15 1989

U. S. FISH AND WILDLIFE SERVICE  
PATUXENT ANALYTICAL CONTROL FACILITY

QUALITY ASSURANCE REPORT

RE:# 5652      REGION : 4      REGIONAL ID 88-4-041

THE ANALYSES ON THE ABOVE MENTIONED SAMPLES WERE PERFORMED AT:

TEXAS A&M RESEARCH FOUNDATION  
10 SOUTH GRAHAM RD  
COLLEGE STATION, TX 77840

THIS LABORATORY WAS SUBJECTED TO A RIGOROUS EVALUATION PROCESS PRIOR TO THE AWARDED OF IT'S CONTRACT. A PANEL OF FISH AND WILDLIFE SERVICE SCIENTISTS CERTIFIED IT TO BE TECHNICALLY QUALIFIED TO PERFORM THE ANALYSES REPORTED HERE. IN ADDITION WE HAVE CONTINUED TO CLOSELY MONITOR THIS LABORATORY'S PERFORMANCE AND HAVE FOUND THE PRECISION AND ACCURACY OF THEIR WORK REMAINS ACCEPTABLE. WE HAVE GREAT CONFIDENCE IN THE ACCURACY OF THESE DATA.

*John F. Moore 5-12-89*  
JOHN F. MOORE

**TOC**  
**ST. ANDREW BAY**

U. S. Fish and Wildlife Service  
Patuxent Analytical Control Facility

Quality Assurance Report

RE Lot# 134

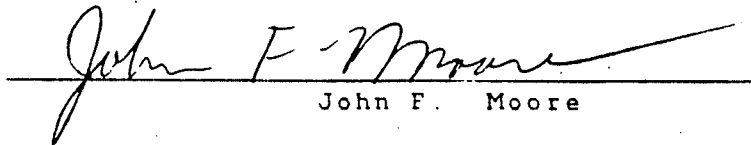
Region 4

Region ID R4-85-5 - SD Andrew Bay

The analyses on the above mentioned samples were performed at:

The Mississippi State Chemical Laboratory, Box CR, Mississippi State, MS 39762.

This laboratory was subjected to a rigorous evaluation process prior to the awarding of it's contract. A panel of Fish and Wildlife Service scientists certified it to be technically qualified to perform the analyses reported here. In addition we have continued to closely monitor this laboratory's performance and have found the precision and accuracy of their work remains acceptable. We have great confidence in the accuracy of these data.

  
John F. Moore

JUN 24

U. S. FISH AND WILDLIFE SERVICE  
PATUXENT ANALYTICAL CONTROL FACILITY

QUALITY ASSURANCE REPORT

RE:# 5410      REGION : 4      REGIONAL ID R4-86-015

THE ANALYSES ON THE ABOVE MENTIONED SAMPLES WERE PERFORMED AT:

THE ENVIRONMENTAL TRACE SUBSTANCES RESEARCH CENTER  
ROUTE 3  
COLUMBIA, MISSOURI 65201

THIS LABORATORY WAS SUBJECTED TO A RIGOROUS EVALUATION PROCESS PRIOR TO THE AWARDED OF IT'S CONTRACT. A PANEL OF FISH AND WILDLIFE SERVICE SCIENTISTS CERTIFIED IT TO BE TECHNICALLY QUALIFIED TO PERFORM THE ANALYSES REPORTED HERE. IN ADDITION WE HAVE CONTINUED TO CLOSELY MONITOR THIS LABORATORY'S PERFORMANCE AND HAVE FOUND THE PRECISION AND ACCURACY OF THEIR WORK REMAINS ACCEPTABLE. WE HAVE GREAT CONFIDENCE IN THE ACCURACY OF THESE DATA.

*John F. Moore 6-22-88*  
JOHN F. MOORE

SOUTHERN Flounder COPY  
Whole Body

U. S. FISH AND WILDLIFE SERVICE  
PATUXENT ANALYTICAL CONTROL FACILITY

FEB 9 1987

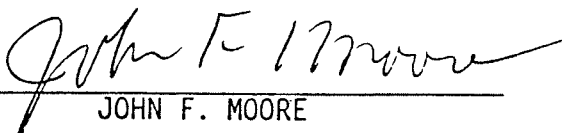
QUALITY ASSURANCE REPORT

RE:# 5210      REGION : 4      REGIONAL ID R4-87-02

THE ANALYSES ON THE ABOVE MENTIONED SAMPLES WERE PERFORMED AT:

THE ENVIRONMENTAL TRACE SUBSTANCES RESEARCH CENTER  
ROUTE 3  
COLUMBIA, MISSOURI 65201

THIS LABORATORY WAS SUBJECTED TO A RIGOROUS EVALUATION PROCESS PRIOR TO THE AWARDED OF IT'S CONTRACT. A PANEL OF FISH AND WILDLIFE SERVICE SCIENTISTS CERTIFIED IT TO BE TECHNICALLY QUALIFIED TO PERFORM THE ANALYSES REPORTED HERE. IN ADDITION WE HAVE CONTINUED TO CLOSELY MONITOR THIS LABORATORY'S PERFORMANCE AND HAVE FOUND THE PRECISION AND ACCURACY OF THEIR WORK REMAINS ACCEPTABLE. WE HAVE GREAT CONFIDENCE IN THE ACCURACY OF THESE DATA.

  
\_\_\_\_\_  
JOHN F. MOORE

U. S. FISH AND WILDLIFE SERVICE  
PATUXENT ANALYTICAL CONTROL FACILITY

QUALITY ASSURANCE REPORT

RE:# 5411      REGION : 4      REGIONAL ID R4-86-030

THE ANALYSES ON THE ABOVE MENTIONED SAMPLES WERE PERFORMED AT:

THE MISSISSIPPI STATE CHEMICAL LABORATORY  
BOX CR  
MISSISSIPPI STATE, MISSISSIPPI 39762

THIS LABORATORY WAS SUBJECTED TO A RIGOROUS EVALUATION PROCESS PRIOR TO THE AWARDED OF IT'S CONTRACT. A PANEL OF FISH AND WILDLIFE SERVICE SCIENTISTS CERTIFIED IT TO BE TECHNICALLY QUALIFIED TO PERFORM THE ANALYSES REPORTED HERE. IN ADDITION WE HAVE CONTINUED TO CLOSELY MONITOR THIS LABORATORY'S PERFORMANCE AND HAVE FOUND THE PRECISION AND ACCURACY OF THEIR WORK REMAINS ACCEPTABLE. WE HAVE GREAT CONFIDENCE IN THE ACCURACY OF THESE DATA.

*John F. Moore* 4-4-88  
\_\_\_\_\_  
JOHN F. MOORE

SEATRUT (OFFAL, FILLET, LIVER) - PAH, AH.

U. S. FISH AND WILDLIFE SERVICE  
PATUXENT ANALYTICAL CONTROL FACILITY

JUL 21 1986

QUALITY ASSURANCE REPORT

RE:# 5411      REGION : 4      REGIONAL ID R4-86-030

THE ANALYSES ON THE ABOVE MENTIONED SAMPLES WERE PERFORMED AT:

THE ENVIRONMENTAL TRACE SUBSTANCES RESEARCH CENTER  
ROUTE 3  
COLUMBIA, MISSOURI 65201

THIS LABORATORY WAS SUBJECTED TO A RIGOROUS EVALUATION PROCESS PRIOR TO THE AWARDING OF IT'S CONTRACT. A PANEL OF FISH AND WILDLIFE SERVICE SCIENTISTS CERTIFIED IT TO BE TECHNICALLY QUALIFIED TO PERFORM THE ANALYSES REPORTED HERE. IN ADDITION WE HAVE CONTINUED TO CLOSELY MONITOR THIS LABORATORY'S PERFORMANCE AND HAVE FOUND THE PRECISION AND ACCURACY OF THEIR WORK REMAINS ACCEPTABLE. WE HAVE GREAT CONFIDENCE IN THE ACCURACY OF THESE DATA.

*John F. Moore* 7-14-86  
\_\_\_\_\_  
JOHN F. MOORE

METALS - Spotted Seatrout - Offal, Liver, Fillet

U. S. FISH AND WILDLIFE SERVICE  
PATUXENT ANALYTICAL CONTROL FACILITY

QUALITY ASSURANCE REPORT

RE: # 169      REGION : 4      REGIONAL ID # 4-85-26 (St Andrew Bay)

THE ANALYSES ON THE ABOVE MENTIONED SAMPLES WERE PERFORMED AT:

THE MISSISSIPPI STATE CHEMICAL LABORATORY  
BOX CR  
MISSISSIPPI STATE, MISSISSIPPI 39762

THIS LABORATORY WAS SUBJECTED TO A RIGOROUS EVALUATION PROCESS PRIOR TO THE AWARDED OF IT'S CONTRACT. A PANEL OF FISH AND WILDLIFE SERVICE SCIENTISTS CERTIFIED IT TO BE TECHNICALLY QUALIFIED TO PERFORM THE ANALYSES REPORTED HERE. IN ADDITION WE HAVE CONTINUED TO CLOSELY MONITOR THIS LABORATORY'S PERFORMANCE AND HAVE FOUND THE PRECISION AND ACCURACY OF THEIR WORK REMAINS ACCEPTABLE. WE HAVE GREAT CONFIDENCE IN THE ACCURACY OF THESE DATA.

  
JOHN F. MOORE

U. S. FISH AND WILDLIFE SERVICE  
NATIONAL AQUACULTURAL CONTROL FACILITY

QUALITY ASSURANCE RECEIPT

RE:# 169

REGION : 4


REGIONAL ID R4-85-26

(SD Andrew E. King)  
Sediments

THE ANALYSES ON THE ABOVE MENTIONED SAMPLES WERE PERFORMED AT:

THE ENVIRONMENTAL TRACE SUBSTANCES RESEARCH CENTER  
ROUTE 3  
COLUMBIA, MISSOURI 65201

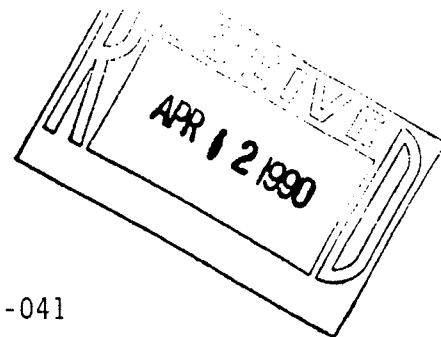
THIS LABORATORY WAS SUBJECTED TO A RIGOROUS EVALUATION PROCESS PRIOR TO THE AWARDED OF ITS CONTRACT. A PANEL OF FISH AND WILDLIFE SERVICE SCIENTISTS CERTIFIED IT TO BE TECHNICALLY QUALIFIED TO PERFORM THE ANALYSES REPORTED HERE. IN ADDITION WE HAVE CONTINUED TO CLOSELY MONITOR THIS LABORATORY'S PERFORMANCE AND HAVE FOUND THE PRECISION AND ACCURACY OF THEIR WORK REMAINS ACCEPTABLE. WE HAVE GREAT CONFIDENCE IN THE ACCURACY OF THESE DATA.

  
\_\_\_\_\_  
JOHN F. MOORE

PARTIAL REPORT

U. S. FISH AND WILDLIFE SERVICE  
PATUXENT ANALYTICAL CONTROL FACILITY

QUALITY ASSURANCE REPORT



RE: 5652

REGION: 4

REGIONAL ID: 88-4-041

THE ANALYSES ON THE ABOVE MENTIONED SAMPLES WERE PERFORMED AT:

THE ENVIRONMENTAL TRACE SUBSTANCES RESEARCH CENTER  
ROUTE 3  
COLUMBIA, MISSOURI 65201

AFTER A THOROUGH REVIEW OF THE REPORTS ISSUED BY THE LABORATORY, I REPORT  
THE FOLLOWING OBSERVATIONS AND CONCLUSIONS:

THE ACCURACY, AS MEASURED BY SPIKE RECOVERY AND REFERENCE MATERIAL ANALYSIS,  
WAS GENERALLY ACCEPTABLE. RECOVERY OF TIN WAS UNACCEPTABLE AND THE TIN DATA  
SHOULD NOT BE USED. AVERAGE RECOVERY FOR SPIKED SAMPLE ANALYSES IS GIVEN IN  
TABLE 1.

THE PRECISION, AS MEASURED BY DUPLICATE SAMPLE ANALYSIS, WAS GENERALLY  
ACCEPTABLE. IN ONE DUPLICATE, THE DEGREE OF DUPLICATION FOR LEAD WAS  
UNACCEPTABLE. THIS MIGHT BE DUE TO THE PRESENCE OF NON HOMOGENEOUS LEAD  
PARTICLES IN THE SAMPLE. THE SAMPLE DUPLICATED WELL FOR THE OTHER ANALYTES  
AND THE DISCREPANCY IS PROBABLY NOT CAUSE FOR CONCERN. AN ESTIMATE OF THE  
95 % CONFIDENCE INTERVAL FOR THE METHODS USED IN THESE ANALYSES IS GIVEN IN  
TABLE 2.

*Clifford P. Lee* 4-8-90  
-----  
QUALITY ASSURANCE OFFICER      DATE

**SN, H G, A S, S E, I C P  
ST. ANDREW BAY**



UNIVERSITY OF MISSOURI

Environmental Trace Substances Research Center

Route 3  
Columbia, Missouri 65203  
Telephone (314) 882-2151

## % MOISTURE

For animal tissue and sediments of sufficient size, moisture was determined by placing a weighed aliquot of the sample in a Fisher Isotemp oven and drying at 103-105°C. The dried sample was then weighed and the data entered into a computer program to generate the % moisture and final report.

Plants, and samples too small for oven dried moisture determination had the % moisture calculated from the moisture lost during the freeze-drying in the Labcono Freeze-Dryer 8. The data was entered into a computer program to generate a % moisture and final report.



UNIVERSITY OF MISSOURI

Environmental Trace Substances Research Center

Route 3  
Columbia, Missouri 65203  
Telephone (314) 882-2151

### HOMOGENIZATION

Large tissue samples, such as whole fish, were first run through a meat grinder one or more times depending on the size of the sample. An aliquot of the ground sample was weighed and frozen. For smaller tissue samples and plant samples the entire sample was weighed and then frozen. For sediments, the sample was mixed and an aliquot weighed and frozen. The frozen samples were placed in a Labcono Freeze Dryer 8 until the moisture had been removed. The dry samples were then weighed and further homogenized using a blender, or Spex Industries, Inc. Model 8000 mixer/mill with tungsten-carbide vial and balls.

COLUMBIA KANSAS CITY ROLLA ST. LOUIS

an equal opportunity institution



UNIVERSITY OF MISSOURI

Environmental Trace Substances Research Center

Route 3  
Columbia, Missouri 65203  
Telephone (314) 882-2151

### NITRIC - PERCHLORIC DIGESTION - (SELENIUM)

Approximately 0.5 g. of sample was weighed into a freshly cleaned 100 ml. quartz Kjeldahl flask. (Sediment samples and samples containing a high percent of silica were digested in 100 ml. teflon breakers.) For water samples, 50 ml. of sample were measured into a teflon beaker. Slowly 15 ml. of concentrated sub-boiled  $\text{HNO}_3$  and 2.5 ml. of concentrated sub-boiled  $\text{HClO}_4$  were added. Foaming may occur with some samples. If the foaming started to become excessive, the container was cooled in a beaker of cold water. After the initial reaction had subsided, the sample was placed on low heat until the evolution of dark red fumes had ceased. Gradually, the heat was increased until the  $\text{HNO}_3$  began refluxing, samples were allowed to reflux overnight. (This decreased the chance for charring during the reaction with  $\text{HClO}_4$ .) After the refluxing, the heat was gradually increased until the  $\text{HNO}_3$  had been driven off, and the reaction with  $\text{HClO}_4$  had occurred. When dense white fumes from the  $\text{HClO}_4$  were evident, the samples were removed from the heat and allowed to cool. Two ml. of concentrated sub-boiled  $\text{HCl}$  were added. The flasks were replaced on the heat and warmed until the containers were hot to the touch or started to boil. They were removed from the heat, and 5-10 ml. of deionized water were added. Samples were allowed to cool. They were then diluted using deionized water in a 50 ml. volumetric flask and transferred to clean, labeled, 2 oz. polyethylene bottles.



UNIVERSITY OF MISSOURI

Environmental Trace Substances Research Center

Route 3  
Columbia, Missouri 65203  
Telephone (314) 882-2151

### NITRIC - PERCHLORIC DIGESTION - (ARSENIC)

Approximately 0.5 g. of sample was weighed into a freshly cleaned 100 ml. Kjeldahl flask. (Sediment samples and samples containing a high percent of silica were digested in 100 ml. teflon beakers.) For water samples, 50 ml. of sample were measured into a teflon beaker. Slowly 15 ml. of concentrated sub-boiled  $\text{HNO}_3$  and 2.5 ml. of concentrated sub-boiled  $\text{HClO}_4$  were added. Foaming may occur with some samples. If the foaming started to become excessive, the container was cooled in a beaker of cold water. After the initial reaction had subsided, the sample was placed on low heat until the evolution of dark red fumes had ceased. Gradually, the heat was increased until the  $\text{HNO}_3$  had been driven off, and the reaction with  $\text{HClO}_4$  had occurred. After this reaction, the samples were heated approximately 5 minutes, after dense white fumes from the  $\text{HClO}_4$  were evident. The samples were removed from the heat and allowed to cool. Samples were diluted using deionized water in 50 ml. volumetric flasks and transferred to clean, labeled, 2 oz. polyethylene bottles.

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### NITRIC - PERCHLORIC DIGESTION - (ICP)

Approximately 0.5 g. of sample was weighed into a freshly cleaned 100 ml. quartz Kjeldahl flask. (Sediment samples and samples containing a high percent of silica were digested in 100 ml. teflon beakers.) For water samples, 50 ml. of sample were measured into a teflon beaker. Slowly 15 ml. of concentrated sub-boiled  $\text{HNO}_3$  and 2.5 ml. of concentrated sub-boiled  $\text{HClO}_4$  were added. Foaming may occur with some samples. If the foaming started to become excessive, the container was cooled in a beaker of cold water. After the initial reaction had subsided, the sample was placed on low heat until the evolution of dark red fumes had ceased. Gradually, the heat was increased until the  $\text{HNO}_3$  began refluxing, samples were allowed to reflux overnight. (This decreased the chance for charring during the reaction with  $\text{HClO}_4$ .) After the refluxing, the heat was gradually increased until the  $\text{HNO}_3$  had been driven off, and the reaction with  $\text{HClO}_4$  had occurred. When dense white fumes from the  $\text{HClO}_4$  were evident, the samples were removed from the heat and allowed to cool. Two ml. of concentrated sub-boiled  $\text{HCl}$  were added. The flasks were replaced on the heat and warmed until the containers were hot to the touch or started to boil. They were removed from the heat, and 5-10 ml. of deionized water were added. Samples were allowed to cool. They were then diluted using deionized water in a 50 ml. volumetric flask and transferred to clean, labeled, 2 oz. polyethylene bottles.

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### NITRIC REFLUX DIGESTION FOR MERCURY

Approximately 0.5 g. of sample was weighed into a freshly cleaned 50 ml. round bottom flask with 24/40 ground glass neck. For waters, 10 ml. of sample were measured into the flask. Five ml. of concentrated sub-boiled  $\text{HNO}_3$  were added and the flask was placed under a 12 inch water-cooled condenser with water running through the condenser. The heat was turned up to allow the  $\text{HNO}_3$  to reflux no more than 1/3 the height of the columns. Samples were allowed to reflux for two hours. Then the heat was turned off and the samples allowed to cool. The condensers were rinsed with 1% v/v HCl and the flasks removed. The samples were diluted with 1% v/v HCl in a 50 ml. volumetric flask and then transferred to clean, labeled, 2 oz. flint glass bottles.



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## ARSENIC AND SELENIUM BY HYDRIDE

The Varian VGA-76 hydride generation accessory was mounted on either a Perkin-Elmer Model 603 AA or Model 3030 (B) AA. Electrodeless Discharge lamps (EDL) were used. The instrument and EDL settings were taken from the instrument manuals. The burner mount for a Perkin-Elmer Model 10 Hydride generator was modified slightly to hold the Varian quartz cell. The cell was aligned in the light path of the burner chamber and a very lean flame was used for heating the cell. The two stock solutions were 50% v/v sub-boiled HCl and 0.6%  $\text{NaBH}_4$  in 0.5% NaOH for Selenium and concentrated sub-boiled HCl and 1%  $\text{NaBH}_4$  in 0.5% NaOH for Arsenic. Samples were diluted with 10% v/v sub-boiled HCl. Standards were prepared by dilution of Fisher 1000 ppm stock with 10% v/v sub-boiled HCl in the range of 0 to 20 PPB. The instrument was standardized to read directly in PPB using  $S_1 = 5.00$  and  $S_2 = 20.00$ . After standardization, the standardization was checked by reading other standards such as 2.00, 10.00 and 15.00 PPB and an instrumental quality control sample with a known value. If the standards and quality control were acceptable, the detection limit was determined by reading the zero standard 10 times, and twice the standard deviation of the mean was used as the detection limit. Samples were analyzed by taking an integrated reading for 3 seconds after the plateau was reached for the sample. This occurred approximately 45 seconds after the sample tube was placed in the sample. Standardization was checked every 8-15 samples and approximately 10% of the samples were checked by the method of additions to monitor matrix effects. Matrix effects were usually not significant with the VGA-76. The data was corrected for drift of the standard curve and entered into the AA calculation program. This program corrected for blank, dilution, sample weight, sample volume and recorded the data in the LIMS database for report generation.

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### MERCURY - COLD VAPOR ATOMIC ABSORPTION

Equipment used for Cold Vapor Atomic Absorption include: Perkin-Elmer Model 403 AA; Perkin-Elmer Model 056 recorder; Technicon Sampler I; Technicon Pump II; a glass cell with quartz windows and capillary tube for entry and exit of the mercury vapor; and a liquid-gas separator. The samples were placed in 4 ml. sample cups at least 3/4 full. The samples were mixed with hydroxylamine for preliminary reduction, then stannous chloride for reduction to the mercury vapor. The vapor was separated from the liquid and passed through the cell mounted in the light path of the burner compartment. The peaks were recorded and the peak heights measured. The standardization was done with at least 5 standards in the range of 0 to 10 ppb. The correlation coefficient was usually 0.9999 or better and must have been at least 0.999 to have been acceptable. A standard was run every 8-10 samples to check for drift in the standardization. This was usually less than 5%. Standards were preserved with 10% v/v  $\text{HNO}_3$ , 1% v/v  $\text{HCl}$  and 0.05% w/v  $\text{K}_2\text{Cr}_2\text{O}_7$ . The solution concentrations were calculated and the data entered into the AA calculation program which corrected for blank, dilution, sample weight, sample volume and entered the data into the LIMS system for report generation.



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### INDUCTIVELY COUPLED PLASMA (ICP)

The instrument used for ICP analysis was a Jarrell-Ash Model 1100 Mark III with 40 analytical channels, controlled by a Digital Equipment Company (DEC) 11/23+ computer with two RL02 disk drives, DEC VT100 terminal, and DEC LA120 decwriter III. The instrument was standardized with a series of seven standards containing 36 elements. After the standardization, the detection limit was determined by taking ten integrations of the zero standard; three times the standard deviation of the mean was used as the detection limit. Instrumental quality control samples were then analyzed to check the ICP operation. If the values were acceptable, the samples were then analyzed. Standards were run every 10-15 samples to check for drift. If the drift was more than 5%, the instrument was restandardized. After the analyses were completed, the data were transferred to the Perkin-Elmer LIMS 2000 computer for calculation. The final detection limit for each element was further increased by 4% of the magnitude of the spectral interferences from the other elements. The data were checked before calculation to correct for possible errors in sample number, weight, volumes and dilution. The data were calculated using the ICP calculation program written by ETSRC computer staff, which corrected for blanks, standard drift, spectral interferences, sample weight, sample volume, and dilution. After the quality control was reviewed, a final report was generated using a Hewlett-Packard laser jet printer.

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### NITRIC DIGESTION FOR GRAPHITE FURNACE

Approximately 0.5 g. of sample was weighed into a freshly cleaned 100 ml. Kjeldahl flask. (Sediment samples and samples containing a high percent of silica were digested in 100 ml. teflon beakers.) For water samples, 50 ml. of sample were measured into a teflon beaker. Slowly, 15 ml. of sub-boiled  $\text{HNO}_3$  were added. Foaming may occur with some samples. If the foaming started to become excessive, the flask was cooled in a beaker of cold water. The samples were placed on low heat until the initial reaction and evolution of dark red fumes had ceased. Gradually, the heat was increased until the volume was reduced to approximately 2 ml. The sample was removed from the heat and allowed to cool. Samples were diluted using deionized water in a 50 ml. volumetric flask and transferred to clean, labeled, 2 oz. polyethylene bottles.



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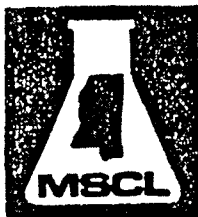
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### GRAPHITE FURNACE AA

The instruments used for graphite furnace AA, were either a Perkin-Elmer Model 3030B with Model HGA-500 graphite furnace, Model AS-40 autosampler and Model 056 recorder, or the Perkin-Elmer Model 5100 Zeeman with Model HGA-600 graphite furnace, Model AS-60 autosampler and Model 7300 computer. The conditions for a particular element were set up according to the instruction manual. The L'vov platform and appropriate matrix modifier were used. A standard curve and known quality control sample were run to check the instrument operation. The method of standard additions was used on a minimum of 1 out of 5 samples. If the average slopes for the standard additions gave a %RSD of 5% or less then the average slope was used to calculate the sample concentrations. If the average slope was not acceptable then the samples all had to be run using the method of standard additions. After calculating the solution concentrations, the data were entered into a computer program that corrected for blank, dilution, sample weight and volume, and entered the data into the LIMS data base for report generation.





MISSISSIPPI  
STATE CHEMICAL LABORATORY

BOX CR - MISSISSIPPI STATE, MISSISSIPPI 39762



August 24, 1989

Mr. Danny Day  
Stickel Building/Chemistry  
Patuxent Wildlife Research Center  
U.S. Fish and Wildlife Service  
Route 197  
Laurel, MD 20708

Dear Danny:

Enclosed are analytical results for one batch of samples submitted by the U.S. Fish and Wildlife Service (Catalog # 5652, Batch # 88-4-041, Order # 85800-88-30137). The samples were analyzed by Methods 2 and 4. Descriptions are enclosed.

Please call if you have any questions.

Sincerely,

Larry G. Lane  
Principal Investigator

Method 1. Analysis For Organochlorine Pesticides and PCBs In Animal and Plant Tissue.

Ten gram tissue samples are thoroughly mixed with anhydrous sodium sulfate and soxhlet extracted with hexane for seven hours. The extract is concentrated by rotary evaporation; transferred to a tared test tube, and further concentrated to dryness for lipid determination. The weighed lipid sample is dissolved in petroleum ether and extracted four times with acetonitrile saturated with petroleum ether. Residues are partitioned into petroleum ether which is washed, concentrated, and transferred to a glass chromatographic column containing 20 grams of Florisil. The column is eluted with 200 ml 6% diethyl ether/94% petroleum ether (Fraction I) followed by 200 ml 15% diethyl ether/85% petroleum ether (Fraction II). Fraction II is concentrated to appropriate volume for quantification of residues by packed or capillary column electron capture gas chromatography. Fraction I is concentrated and transferred to a Silicic acid chromatographic column for additional cleanup required for separation of PCBs from other organochlorines. Three fractions are eluted from the silicic acid column. Each is concentrated to appropriate volume for quantification of residues by packed or megabore column, electron capture gas chromatography. PCBs are found in Fraction II.

Method 2. Analysis For Organochlorine Pesticides and PCBs In Soil and Sediment.

Twenty-five gram soil or sediment samples are extracted with acetone followed by hexane, by allowing to soak one hour in each with intermittent shaking. The combined extracts are centrifuged and decanted into a separatory funnel containing sufficient water to facilitate partitioning of residues into hexane portion. The hexane is washed twice with water and concentrated to appropriate volume for transfer to a 1.6 gram Florisil mini-column topped with 1.6 grams sodium sulfate. Residues are eluted from the column in two elution fractions. Fraction I consists of 12 milliliters hexane followed by 12 milliliters of 1% methanol in hexane, and Fraction II consists of an additional 24 milliliters of 1% methanol in hexane. If additional cleanup is required to separate PCBs from other organochlorines in Fraction I, further chromatography on a Silicic acid column is performed. Quantification of residues in the two Florisil fractions and three Silicic acid fractions is by packed or megabore column, electron capture gas chromatography.

Method 3. Analysis For Aliphatic and Polynuclear Aromatic Hydrocarbons In Animal and Plant Tissue.

A sample of appropriate size (i.e. 15 grams animal or plant tissue, 2 grams adipose, 5 grams eggs) is digested in 6N aqueous potassium hydroxide for 24 hours at 35 °C. Cool digestate thoroughly in an ice bath and carefully neutralize with glacial acetic acid. Extract the neutralized reaction mixture three times with methylene chloride; concentrate the combined extracts to near dryness and reconstitute in petroleum ether for transfer to a 20 gram 1% deactivated silica gel column, topped with 5 grams neutral alumina. Aliphatic and polynuclear aromatic hydrocarbon residues are separated by eluting aliphatics from the column with 100 ml petroleum ether (Fraction I) followed by elution of aromatics using first, 100ml 40% methylene chloride/60% petroleum ether, then 50 ml methylene chloride (Combined eluates, Fraction II). If needed, Fraction I containing aliphatics is subjected to additional cleanup by concentration and transfer to a deactivated (2% water) Florisil column. Aliphatic residues are eluted from the Florisil column using 200 ml 6% diethyl ether/94% petroleum ether. The eluate is concentrated to appropriate volume for quantification by capillary column, flame ionization gas chromatography. The silica gel Fraction II containing aromatic hydrocarbons is concentrated, reconstituted in methylene chloride, and subjected to gel permeation chromatography (GPC) cleanup prior to quantification by capillary, flame ionization gas chromatography and fluorescence HPLC.

#### Method 4. Analysis For Aliphatic and Aromatic Hydrocarbons In Soil and Sediment.

Twenty gram soil or sediment samples are extracted with acetone, followed by petroleum ether, by allowing to soak one hour in each with intermittent shaking. A final acetone/petroleum ether extraction is done, and the extracts are combined, centrifuged, and transferred to a separatory funnel containing sufficient water to facilitate partitioning of residues into petroleum ether portion. The petroleum ether is washed twice with water and concentrated by Kuderna-Danish to appropriate volume for transfer to a 20 gram 1% deactivated silica gel column, topped with five grams neutral alumina. Aliphatic and polynuclear aromatic hydrocarbon residues are fractionated by eluting aliphatics from the column with 100 ml petroleum ether (Fraction I) followed by elution of aromatics using first, 100 ml 40% methylene chloride/60% petroleum ether, then 50 ml methylene chloride (Combined eluates, Fraction II). If needed, Fraction I containing aliphatics is subjected to additional cleanup by concentration and transfer to a deactivated (2% water) Florisil column. Aliphatic residues are eluted from the Florisil column using 200 ml 6% diethyl ether/94% petroleum ether. The eluate is concentrated to appropriate volume for quantification by capillary column, flame ionization gas chromatography. The silica gel Fraction II containing aromatic hydrocarbons is concentrated, reconstituted in methylene chloride, and subjected to gel permeation chromatographic (GPC) cleanup prior to quantification by capillary, flame ionization gas chromatography and fluorescence HPLC.

Elution Profiles for Florisil, Silica Gel and  
Silicic Acid Column Separations

A. Florisil Column:

1. Fraction I (6% ethyl ether containing 2% ethanol, 94% petroleum ether)

HCB, alpha-BHC, beta-BHC, gamma-BHC, delta-BHC, oxychlordane, heptachlor epoxide, gamma-chlordane, trans-nonachlor, toxaphene, PCB's, o,p'-DDE, alpha-Chlordane, p,p'-DDE, p,p'-DDT, cis-nonachlor, o,p'-DDT, p,p'-DDD, p,p'-DDT, mirex, dicofol, endosulfan I (Split with FII).

2. Fraction II (15% ethyl ether containing 2% ethanol, 85% petroleum ether)

dieldrin, endrin, dacthal, endosulfan I (split with FI), endosulfan II (split with FIII), endosulfan sulfate (split with FIII).

3. Fraction III (50% ethyl ether containing 2% ethanol, 50% petroleum ether)

endosulfan II (split with FII), endosulfan sulfate (split with FII), malathion.

B. Florisil Mini-Column:

1. Fraction I (12 ml hexane followed by 12 ml 1% methanol in hexane)

HCB, gamma-BHC (25%), alpha-BHC (splits with FII),  
trans-nonachlor, o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD  
(splits with FII), o,p'-DDT, p,p'-DDT, mirex,  
cis-nonachlor, cis-chlordane, trans-chlordane, PCB's

2. Fraction II (24 ml 1% methanol in hexane)

gamma BHC (75%), beta-BHC, alpha-BHC (splits with FI),  
delta-BHC, oxychlordane, heptachlor epoxide, toxaphene,  
dicofol, dacthal.

C. Silica Gel:

1. SG Fraction I (100 ml petroleum ether)

n-dodecane, n-tridecane, n-tetradecane, ocylcyclohexane,  
n-pentadecane, nonycyclohexane, n-hexadecane,  
n-heptadecane, pristane, n-octadecane, phytane,  
n-nonadecane, n-eicosane.

2. SG Fraction II (100 ml 40% methylene chloride in petroleum ether followed by 50 ml methylene chloride)

napthalene, fluorene, phenanthrene, anthracene,  
fluoranthrene, pyrene, 1,2-benzanthracene, chrysene, benzo  
[b] fluoranthrene, benzo [k] fluoranthrene, benzo [e]  
pyrene, benzo [a] pyrene, 1,2:5,6-dibenzanthracene, benzo  
[g,h,i] perylene.

D. Silicic Acid:

1. SA Fraction I (20 ml petroleum ether)  
HCB, mirex
2. SA Fraction II (100ml petroleum ether)  
PCB's, p,p'-DDE (splits with SA III)
3. SA Fraction III (20 ml mixed solvent: 1% acetonitrile, 80% methylene chloride, 19% hexane)  
alpha-BHC, beta-BHC, gamma-BHC, delta-BHC, oxychlordane, heptachlor epoxide, gamma-chlordane, trans-chlordane, toxaphene, o,p'-DDE, alpha-chlordane, p,p'-DDE (splits with SAII), o,p'-DDT, cis-nonachlor, o,p'-DDT, p,p'-DDD, p,p'-DDT, dicofol.

**Method 6. Analysis For Chlorinated Hydrocarbon Pesticides And Related Compounds - Micro Method**

This method is necessary when sample size is limited (below 4 g, approximately) and in case of organ tissue as substrate and is a modified version of the method described in Manual of Analytical Methods for the Analysis of Pesticides in Humans and Enviromental Samples, EPA-600/8-80-038, June 1980, Section 5, A (2). It is suitable for adipose, kidney, liver, muscle, brain, and other tissues:

1. Weigh 0.5 g or less of well-mixed tissue into a size 22 Duall tissue grinder.
2. Extract tissue by grinding three times with acetonitrile; the first time being with 4 ml followed by two 2.5 ml portions.
3. Remove the pestle after each grinding and centrifuge, decanting the extract into a 50 ml glass stoppered graduated mixing cylinder.
4. Combine all extracts and record the total volume of the three extracts.
5. Add a volume of PRQ water equivalent to 3.3 times the extract volume. Then add 2 ml saturated NaCl solution.
6. Extract the aqueous acetonitrile mixture with 5 ml hexane by vigorous shaking for 1 minute.
7. Allow layers to separate, and remove the hexane layer with a Pasteur pipet into a 15 ml screw-capped culture tube.
8. Re-extract twice with 2 ml hexane each time, combining the extracts into the culture tube.
9. Concentrate the combined hexane extracts under nitrogen to approximately 0.5 ml volume.
10. Clean-up on a florisil mini-column as described in Method 2, Steps 8, 9, 10. and 11.

Note For brain tissue additional treatment is necessary before column clean-up:

11. Proceed through Steps 1-9 above, add 0.3 ml acetic anhydride and 0.3 ml pyridine, cap tightly and incubate for 30 minutes in a water bath

at 60-65°C.

12. Add 8 ml PRQ water and 1 ml saturated NaCl and extract three times with 2 ml hexane, combining the extracts into a clean tube.
13. Concentrate the combined extracts under nitrogen to about 0.3 ml and proceed with florisil mini-column clean-up. (Step 10)

Note      The following changes in sample handling, particularly column clean-up, should be observed for Kepone analysis:

14. Maintain the integrity of the analyte in sample extracts by insuring that the samples are not allowed to reach dryness during concentration steps. Kepone easily adheres to glass, but the use of polar solvents such as methanol and acetonitrile within the analysis will provide better recoveries of this analyte.
15. Modifications to florisil mini-column clean-up are as follows;
  - \* Following addition of sample to the column, apply a 1ml rinse of 1% methanol in hexane to the sample tube. This rinse should be added after the first phase of the first fraction (12mls hexane) and will insure removal of trace quantities of kepone adhered to glass. Decrease the total volume of the second phase of the first fraction (12mls 1% methanol/hexane) to 11mls.
  - \* Modify the total volume of the second fraction from 24mls to 36mls 1% methanol/hexane. This fraction contains Kepone.
  - \* Concentrate column fractions on N-EVAP and transfer with 1% methanol/hexane to calibrated test tubes. Adjust sample volume to calibrated level and proceed to determination by gas chromatograph.

## Total Organic Carbon Analyses

Texas A & M Research Foundation

Precise measurements of total organic carbon content are necessary for interpreting trace organic contamination. Our laboratory has a number of options for the analysis of organic carbon. Available in our laboratory is a Perkin-Elmer Model 240C Elemental Analyzer, a Leco WR-12 Total Carbon System, an O.I. Corporation Total Carbon System for the wet oxidation of organic matter, and four Craig-type total combustion lines for conversion of organic matter to  $\text{CO}_2$  and its manometric measurement (used mainly for stable isotope analyses preparation). We routinely use the Leco WR-12 Carbon System as the method of choice. This instrument will be calibrated against the total combustion systems for quality control.

For the Leco WR-12 Total Carbon System analysis, sediment subsamples (0.2-0.5 g) are weighed into disposable 5 ml polystyrene beakers and treated with concentrated HCl to remove inorganic carbon (carbonate). Acid is added dropwise until no degassing is observed. The treated samples are then dried at  $50^\circ\text{C}$  in a recirculating oven for 24-36 hours to remove excess acid and moisture. After drying, the sample is quantitatively transferred to a sintered crucible. Iron accelerator and tin coated copper catalyst are added and analyzed by total combustion on the Leco instrument. Organic carbon is converted to  $\text{CO}_2$  and analyzed with a non-dispersive infrared spectrophotometer. Blanks and standards are run on

a daily basis. Leco steel ring carbon standards are commercially available. Every 10th sample is analyzed in duplicate and every 50th sample is run as a triplicate. Periodically samples are combusted at  $>800^{\circ}\text{C}$  in a high vacuum Craig-type combustion system as a check on the combustion efficiency of the Leco system.

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**TRIANGLE LABORATORIES OF RTP, INC.**

# **DATA USER MANUAL**

## **EPA Method 8290**

High Resolution Mass Spectrometry

Polychlorinated Dibenzodioxins  
and Dibenzofurans

**Tissue, Environmental Samples, Chemicals,  
Ash, Dry Pulp, Paper, Wipes  
Serum and Milk**

Analytical Methodology, Data Quality Objectives,  
Deliverables, Data Package Assembly,  
Description and Examples of Calculations.

**PROPRIETARY INFORMATION**



NOTE

For complete information, regarding the  
*Triangle Laboratories of RTP, Inc.*  
analytical methodology please refer to  
the following EPA document:

Method 8290: Polychlorinated Dibenzodioxins (PCDDs)  
and  
Polychlorinated Dibenzofurans (PCDFs)  
by High-Resolution Gas Chromatography/  
High-Resolution Mass Spectrometry (HRGC/HRMS)

United States Environmental Protection Agency  
Washington, D.C. 20460

September 1994  
Revision O



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NOTE: FOR THE ADDITIONAL INFORMATION CONTAINED IN SECTIONS 3, 4, & 5,  
CONTACT TRIANGLE LABORATORIES OF RTP, INC.

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**Section 1**

**Foreword**

The purpose of this User Manual is to provide details pertaining to the analytical methodology, data quality objectives, the structure of the data package and the calculations used to generate the results submitted with each Sample Data Package. All data packages are assembled in a manner allowing the Data User to recalculate the reported results independently.

Section 2

Analytical Methodology

2.1 Introduction

Method 8290 (Revision 0, November 1990) uses carbon-13 isotopically labeled internal standards (isotope-dilution) for the quantitation of PCDDs/PCDFs by high resolution gas chromatography/high resolution mass spectrometry. Quantitation of the tetra through octachlorinated dibenzo-p-dioxins and dibenzofurans can be performed on a wide variety of environmental matrices with detection levels in the low part-per-trillion (ppt) to part-per-quadrillion (ppq). This new version of the User's Manual, which replaces yt-6 2378X, defines matrices specific to Method 8290. Other PCDD/PCDF methods such as Method 1613, 23 and 8280-CLP are described in separate user's manuals.

The modifications to Method 8290 that Triangle Labs has implemented primarily concern the number (from 11 to 18) of the labeled standards used throughout the procedure and the chronology of addition of the 18 carbon-labeled PCDD/PCDF standards to the sample. Matrices listed below have nine labeled PCDD/PCDF congeners used as internal standards, five labeled PCDD/PCDF congeners are used as surrogate standards, two labeled PCDD/PCDF congeners are used as recovery standards and two labeled HxCDFs are used as alternate standards.

Samples analyzed only for the tetrachlorinated isomers will be fortified with the full set (tetra- through octachlorinated) of standard compounds. The selection of the labeled standards allows at least one carbon-labeled internal standard per class of chlorination (tetra- through octachlorinated) and per class of compounds (dioxins, furans) to be used to characterize and quantify the fifteen 2,3,7,8-substituted PCDD/PCDF congeners (as well as OCDD and OCDF) in addition to reporting the total concentrations of PCDDs and PCDFs.

The method can be used for a variety of matrices including, but not limited to, those listed below (see Table 10 for method calibration limits and sample sizes):

sludge	water	tissue
soil	aqueous waste	fish
fuel oil	PUF	adipose
still bottom	wipes	blood
chemical	ash	milk
sediment	NAPL	effluents

2.1.1 PUF Samples (Figure 1)

PUF samples are normally sampled according to procedures listed in Method TO9. The method of analysis is usually Method 8290.

The PUF sample fortification scheme consists of the addition of five labeled surrogate standards to the sampling module before the sampling session. When the samples are returned to the laboratory for analysis the nine labeled internal standards are spiked on the PUF (and associated filter) before extraction. Following the extraction, two labeled alternate standards are added to the extract before splitting the sample in two equal portions. The concentrations of the internal and alternate standards are determined by using the recovery standards added to the cleaned up sample extract before GC/MS analysis (Section 2.3). This fortification scheme provides the Data User with valuable information regarding the extraction and cleanup procedure efficiencies. The sampling efficiency can be determined from the recovery of the surrogate standards which are quantitated against the internal standards.

### 2.1.2 All Other Matrices (Figures 2 and 3)

All other sample fortification schemes consist in the addition of the internal standards at the extraction step while the surrogate and alternate standards are added to the extract before the cleanup procedure. The concentrations of all the labeled standards (internal, surrogate and alternate) are determined by using the recovery standards added to the cleaned up sample extract before GC/MS analysis (Section 2.3). This fortification scheme provides the Data User with valuable information regarding the cleanup procedure efficiencies as well as the overall (extraction and cleanup) method efficiencies.

### 2.1.3 Sample Data Summary Topsheet

The format used to report the data includes two pages. On the first page (Figure 4) of the Sample Data Summary Topsheet, the concentrations of the 2,3,7,8-substituted PCDD/PCDF congeners are displayed first for the specific dibenzodioxin isomers, the specific dibenzofuran isomers and then for each homologous series. The second page (Figure 5) of the Sample Data Summary Topsheet reports the concentration and percent recoveries of the labeled standards. The hexachlorinated congeners for which more than one carbon-labeled isomer is used (e.g.,  $^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDD and  $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD) are distinguished by specifying on the sample data summary sheet the site of substitution for three of the chlorine atoms ( $^{13}\text{C}_{12}$ -HxCDD 678 =  $^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDD).

## 2.2 Sample Handling

### 2.2.1 Sample Delivery and Storage

Upon receipt, the samples are stored in a refrigerator maintained at 4°C. An internal chain-of-custody form is pre-

pared while recording the sample IDs inside the "Sample Receiving Log Book" (a copy of which is provided in the Document Control section of the data package). In addition to the customer sample ID, Triangle Laboratories assigns an internal sample ID obtained by using the "Sample Receiving Log Book" serial number, the page where the samples are recorded and the page entry number (e.g., 7-139-1 = Log Book No 7, Log Book Page 139 and first entry on that page). Upon receipt of the samples, a Triangle Laboratory Project Number is issued, which is used for tracking the batch of samples and for invoicing purposes. Please refer to this TLI Project Number when questions are submitted about the analytical results.

## 2.2.2 Sample Preparation and Fractionation

### 2.2.2.1 Sample Fortification

All low-level, non-PUF samples (including the quality control and laboratory method blank samples) are fortified with 2 ng of the tetra- through heptachlorinated internal, surrogate and alternate standards and 4 ng of the octachlorinated dibenzodioxin internal standard. High-level samples are processed with five times the aforementioned levels of PCDD/PCDF labeled standards. The fortifications are accomplished by using the sample fortification solution described in Table 1. (The quantitation relationships of the unlabeled analytes and labeled internal standards are presented in Tables 7 and 8.)

Note that for water samples (if applicable), the sample fortification solution is dissolved in acetone (1.5 mL) before spiking the samples. Efforts are made to allow the spiked standard compounds to equilibrate with the indigenous analytes.

PUF samples are fortified with 0.5 ng of the tetra- through heptachlorinated surrogates prior to sampling. Prior to extraction, PUF samples are fortified with 0.5 ng of the tetra- through heptachlorinated internal standards and 1.0 ng of the octachlorinated dibenzodioxin internal standard. The fortifications are accomplished by using the sample fortification solution shown in Table 1. (The quantitation relationships of the unlabeled analytes, labeled internal standard and surrogate standards are described in Tables 7, 8 and 9 respectively.)

### 2.2.2.2 Sample Extraction/Fractionation

Unless requested otherwise, the samples are prepared using the methods described in Method 8290 analytical protocols. Typically, solid samples are extracted by using toluene in a Soxhlet/Dean-Stark extractor apparatus for 16 hours, PUF samples are extracted by using toluene in a Soxhlet apparatus for 16 hours and aqueous samples are extracted with

methylene chloride in a separatory funnel. Note that the the extracting solvent may change depending on the matrix type.

The sample extracts are then washed with concentrated sulfuric acid followed by concentrated sodium hydroxide. This acid/base wash is not normally needed for PUF extracts. The concentrated residue is then fractionated with a series of column cleanups including Biosil and alumina columns. The carbon column used in the final cleanup step is prepared by mixing Celite 545 and AX-21 carbon.

Modifications of the cleanup procedure may be necessary for complex samples. A multilayered acid/base-impregnated silica gel column may be used between the acid/base wash and the alumina column. Larger alumina (or silica gel) columns may also be used to process samples that present large quantities of co-extractants. Please refer to the Document Control section (Analyst notes) and Case Narrative for specific details on the procedure (or deviations from the procedure) that was followed during the handling of your samples.

### 2.2.3 Quality Control Samples

A laboratory method blank -- identified as the TLI Blank -- is prepared along with each batch of samples. One such sample per 20 field samples (or less) of a given matrix is prepared.

When requested, a matrix spike (MS) and matrix spike duplicate (MSD) quality control samples are prepared. They are selected from the sample(s) specified in the Case Narrative and fortified with the 17 unlabeled analytes listed in Table 2. The fortification levels for low-level samples are 0.4 ng of the tetrachlorinated isomers, 2 ng of the penta- through heptachlorinated isomers and 4 ng of the octachlorinated isomers. High-level samples are fortified with 2 ng of the tetrachlorinated isomers, 10 ng of the penta- through heptachlorinated isomers and 20 ng of the octachlorinated isomers. When requested, a duplicate sample (DUP) is extracted and analyzed.

Matrix spike and matrix spike duplicates are not performed for PUF samples since each sample is unique. However at the client's request, a lab control spike (LCS) sample can be prepared. A LCS sample consists of a blank PUF which is fortified with a solution that contains the 17 unlabeled analytes listed in Table 2.

## 2.3 High-Resolution Gas Chromatography / High-Resolution Mass Spectrometry

### 2.3.1 Gas Chromatography

For GC/MS analysis, the final residue is dissolved in 20 uL of a nonane solution containing the recovery standards shown in Table 1. An HP-5890 GC equipped with a fused-silica capillary column, is used for analysis. Two uL of the 20-uL final sample volume are analyzed by using the GC conditions summarized in Table 3.

### 2.3.2 Mass Spectrometry

The samples are analyzed by using either a VG 70S or VG AutoSpec mass spectrometer operated in the selected ion recording mode (SIR), at a resolving power of 10,000 (+/-10%). The Sample Tracking & Management Form specifies the instrument that is actually used for the samples. In addition, the GC/MS file name allows the Data User to identify the type of mass spectrometer used. More specifically, a GC/MS file name starting with the letter "S" (e.g., S010101) indicates that the VG 70S was used to analyze the sample. Similarly, a letter "T", "U" or "W" is used to refer to the VG 70S250 instruments or "X" for the VG AutoSpec instrument. Electron ionization and an ion-chamber temperature of 250°C are used. Perfluorokerosene (PFK) is used to calibrate the SIR mass range. Moreover, one PFK ion per mass descriptor is used as a lock-mass ion to correct mass drifts occurring during the analysis. A list of the various ions monitored is shown in Table 4. In addition to the PCDD/PCDF ions, several ions characteristics of polychlorinated diphenylethers (PCDPEs) are monitored simultaneously with PCDFs.

Each instrument is interfaced to a VAX data system, which is used to acquire the data. A "Mass Spectrometer Run Sheet", summarizing the chronological order of the GC/MS analyses, is provided in the Document Control section of the data package.

System performances are described in Section 2.4.

## 2.4 System Performance and Calibration Checks

### 2.4.1 Initial Calibration

The mass spectrometer response is calibrated by using the set of five initial calibration solutions shown in Table 2. Each solution is analyzed once and the analyte relative response factors (RRF) are calculated. The mean RRF from the initial calibration is used for all quantitations.

For the total homologous PCDD/PCDF concentrations (e.g., total HxCDDs), the RRFs are taken, when applicable, as the average of the RRFs for the individual congeners listed in the initial calibration reporting form. Note that when only one isomer is present, a discrepancy may appear between the

reported concentration for the individual isomer and the total, as a result of using a different RRF.

An acceptable calibration must meet the following criteria:

- 1) The percent relative standard deviations for the mean response factors from each of the unlabeled analytes and of the internal, surrogate and alternate standards must be less than 20 or 30 percent depending on the analyte (Table 5).
- 2) The signal-to-noise ratio (S/N) for the GC signals present in every selected ion current profile must be  $\geq 10:1$ .
- 3) The ion abundance ratios must be within the specified control limits (see Table 6).

#### 2.4.2 Continuing Calibration

A continuing calibration is demonstrated at the beginning and end of every 12 hours by injecting two uL of solution number 4 from Table 2. The RRFs are calculated and compared to the mean RRFs obtained during the initial calibration procedure.

The continuing calibration delta RRF (on the data sheets) corresponds to the relative percent difference between the daily RRF and the initial calibration RRF.

An acceptable continuing calibration run must meet the following criteria:

- 1) The measured RRFs (for the unlabeled analytes as well as labeled compounds) obtained during the continuing calibration run must be within 20 or 30 percent depending on the analyte (Table 5) of the mean RRFs established during the initial calibration.
- 2) The RRFs for the continuing calibration at the end of the 12 hour sequence must be within 25 or 35 percent of the mean RRFs from the initial calibration depending on the analyte (Table 5).
- 3) The signal-to-noise ratio (S/N) for the GC signals present in every selected ion current profile must be  $\geq 10:1$ .
- 4) The ion-abundance ratios must be within the allowed control limits listed in Table 6.

#### 2.4.3 Gas Chromatographic Column Performance Check

At the beginning of every 12-hour shift during which samples are analyzed for tetrachlorinated congeners, or tetra-through octachlorinated dibenzodioxins and dibenzofurans, the fused-silica capillary GC column performance is verified by injecting a solution composed of a mixture of selected

PCDD/PCDF congeners that (1) allows the documentation of the chromatographic resolution between 2,3,7,8-TCDD and other close-eluting TCDD isomers ( $\leq 25\%$  valley) on the DB-5 GC column and 2,3,7,8-TCDF and other close-eluting TCDF isomers on the DB-225 GC column and, (2) permits the mass spectrometer operator to identify the various retention time windows for each class of homologous compounds.

#### 2.4.4 Mass Spectrometer Performance

Documentation of the mass spectrometer resolving power is accomplished by recording the peak profile of the high-mass reference signal ( $m/z$  330.9792) obtained during a peak matching experiment by using the low-mass PFK ion at  $m/z$  292.9825 (or lower in mass) as a reference. The format of the peak profile representation allows manual determination of the peak resolution.

#### 2.4.5 Confirmation Analyses

For samples found to contain 2,3,7,8-TCDF, during analysis using a 60-m DB-5 column, the associated sample extracts are analyzed on a second high-resolution GC column (DB-225) also under high-resolution mass spectrometric conditions. A GC column performance run precedes the analysis of the extracts so that the 2,3,7,8-TCDF isomeric specificity can be documented (see Section 3.4.2; Deliverables). The results for 2,3,7,8-TCDF "confirmation" analyses should be used in the final report.

Confirmation analyses are performed by using a five point calibration curve which is validated as is normally done for the full screen analyses.

### 2.5 Identification Criteria

The positive identification criteria used for the characterization of polychlorinated dibenzo-p-dioxins and dibenzofurans are as follows:

- 1) The integrated ion-abundance ratio ( $M^+/M+2$  or  $M+2/M+4$ ) must be within 15 percent of the theoretical value. The acceptable ion-abundance ratio ranges for the identification of chlorine-containing compounds are given in Table 7.
- 2) The retention time for the analytes must be within -1 to +3 seconds of the corresponding  $^{13}C$ -labeled standard.
- 3) The monitored ions shown in Table 4 for an analyte must maximize within 2 seconds of each other.
- 4) The identification of specific isomers that do not have a corresponding  $^{13}C$ -labeled standards (six congeners) is

done by comparison of the relative retention time (RRT) of the analyte to the nearest internal standard retention time with reference (i.e., within 0.005 RRT units) to the comparable RRTs found in the continuing calibration.

- 5) The signal to noise for all monitored ions must be greater than 2.5.
- 6) The confirmation of 2,3,7,8-TCDD and 2,3,7,8-TCDF must satisfy all of the above identification criteria.
- 7) For the identification of PCDFs, no signal greater than 10% of the area of the congener should be found in the corresponding PCDF channels.

## 2.6 Analyte Quantitation

For quantitations, the sum of the peak areas for the two ions monitored (Table 4) is used. When no peak is detected, the noise level, as measured by the intensity of the noise in a clear zone of the chromatogram, is used to calculate the detection limit. Tables 7, 8, and 9 summarize the quantitation relationships for the unlabeled analytes, internal standards and surrogate/alternate standards, respectively.

For example, regardless of the sample type, the percent recoveries of the carbon-labeled tetra- and penta-chlorinated dibenzodioxins internal standards are calculated by using  $^{13}\text{C}_{12}$ -1,2,3,4-TCDD as the recovery standard. The recoveries of higher homologues (hexa- through octachlorinated congeners) are determined relative to  $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD (Table 8).

### Special Notes:

1. The 2,3,7,8-TCDF concentration must be obtained from the confirmation analysis (on the DB-225 column). Otherwise, the DB-5 column result for 2,3,7,8-TCDF constitutes a maximum possible concentration. The 2,3,7,8-TCDD result reported on the DB-225 column represents maximum possible concentration since the column is not capable of 2,3,7,8-TCDD isomer specificity. A confirmation analysis will not be run for 2,3,7,8-TCDF if it is detected below the target detection limit on the DB-5 column.

2. The "total" concentrations given for each class of chlorination (tetra- through octachlorinated) and type of compound (dioxin, furan) represent the summation of the concentrations for all the GC/MS signals that meet the retention time and ion- abundance ratio criteria discussed in Section 2.5. When a confirmation analysis is performed, two sets of "totals" for tetrachlorinated compounds will be available. It is recommended that the totals obtained from

the GC column that provides the lowest value be used unless the difference (e.g., Total TCDD on DB-5 versus Total TCDD on the DB-225) exceeds the QC limit (see Data Quality Objectives).

3. The analyte concentrations reported on the Sample Data Summary Top Sheet and provided with each sample data pack are "RECOVERY CORRECTED". This is a direct consequence of using isotope-dilution mass spectrometry. Thus, there is no need for adjusting the reported analyte concentrations.

4. No corrections for "blank contributions" are performed by Triangle Laboratories.

5. The total concentrations reported for the dioxin and furan homolog groups include the specific 2,3,7,8-isomers. The EMPC (Section 3.3) reported for totals include the "detected" concentrations also.

## 2.7 QA/QC Remarks

When applicable, general deviations from acceptable QA/QC requirements are identified and discussed in the Case Narrative. Comments on the effect of these deviations upon the validity and reliability of the results are also offered. More details on these issues can be found on the QA/QC Remarks Form included inside the Document Control section of the data package. In addition, Section 5 of the User Manual (Data Quality Objectives) provides guidelines regarding cases where samples present unusually low recoveries.

## 2.8 Mono- through Octachlorinated Dibenzodioxins and Dibenzofurans

At the request of the Client, Triangle Laboratories offers the option of monitoring and reporting the mono-, di- and trichlorinated congeners in addition to the tetra- through octachlorinated congeners. However, due to the absence of adequate standard compounds representative of the mono- through trichlorinated congeners, Triangle Laboratories cannot defend the validity or accuracy of the data generated for these lower congeners. The quantitations are performed relative to  $^{13}\text{C}_{12}$ -2,3,7,8-TCDD. The calibration solutions contain several isomers that are used to calculate the relative response factors used for sample analyte quantitations. The RRFs obtained from the continuing calibration are used to compute the concentrations of mono-, di- and trichlorinated congeners.

## 2.9 Toxicity Equivalency Factors

If requested by the Client, the report will contain a tabulation of the toxicity equivalency factors and the

2,3,7,8-TCDD equivalents for each sample. The TEFs are calculated by multiplying the individual and total polychlorinated dibenzodioxin and dibenzofuran concentrations by their respective TCDD equivalency factors and summing these products. There are numerous TEFs currently used which include the EPA (1989) or NATO (International) TEFs listed below. Examples of other TEF types are German, Nordic, California, Ohio and North Carolina TEFs. The client should check with the appropriate agency to see which TEFs are required.

**EPA-1989 or NATO (International) TEFs**

1.00000 x conc. 2,3,7,8-TCDD  
 0.50000 x conc. 1,2,3,7,8-PeCDD  
 0.10000 x conc. 1,2,3,6,7,8-HxCDD  
 0.10000 x conc. 1,2,3,7,8,9-HxCDD  
 0.10000 x conc. 1,2,3,4,7,8-HxCDD  
 0.01000 x conc. 1,2,3,4,6,7,8-HpCDD  
 0.00100 x conc. OCDD

0.10000 x conc. 2,3,7,8-TCDF \*  
 0.05000 x conc. 1,2,3,7,8-PeCDF  
 0.50000 x conc. 2,3,4,7,8-PeCDF  
 0.10000 x conc. 1,2,3,6,7,8-HxCDF  
 0.10000 x conc. 1,2,3,7,8,9-HxCDF  
 0.10000 x conc. 1,2,3,4,7,8-HxCDF  
 0.10000 x conc. 2,3,4,6,7,8-HxCDF  
 0.01000 x conc. 1,2,3,4,6,7,8-HpCDF  
 0.01000 x conc. 1,2,3,4,7,8,9-HpCDF  
 0.00100 x conc. OCDF

-----  
 Total 2,3,7,8-TCDD Toxicity Equivalents

\* The concentration of 2,3,7,8-TCDF is taken from the DB-225 column if available.

Note: The table of TEF originates from the U.S. Environmental Protection Agency (EPA/625/3-89/016; March 1989) "Interim Procedures for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-Dioxins and Dibenzofurans (CDDs and CDFs)".





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August 2, 1995

Ms Diane Bateman  
1612 June Avenue  
Panama City, FL 32045

Dear Ms Bateman,

Enclosed with this letter please find one bound copy of EPA Method 1613, Revision B, and the Chain-of-Custody documents and laboratory summary data tables you requested. The summary data tables contain the dioxin/furan analytical results for the two sediment samples in Fish and Wildlife catalog 4080030. If you have any further questions regarding these analyses or the results please don't hesitate to call me at any time.

Sincerely,

A handwritten signature in cursive script that reads 'Laura Chambers'.

Laura Chambers  
Project Administrator, GERG

enclosure

cc: J. Brooks, GERG  
H. Chambers, GERG  
G. Denoux, GERG  
J. Moore, PACF



NOTE

For complete information, regarding the  
*Geochemical and Environmental Research Group*  
*Texas A & M Univeristy*  
analytical methodology please refer to  
the following EPA document:

Method 1613: Tetra-Through Octachlorinated  
Dioxins and Furans by  
Isotope Dilution HRGC/HRMS  
United States Environmental Protection Agency  
Office of Water  
Engineering and Analysis Division (4303)  
Washington, D.C. 20460

EPA 821-B-94-005  
October 1994  
Revision B



University of South Alabama Analytical Procedures

used by

Dr. Wayne Isphording, Ph.D.  
Tierra Consulting  
5506 Richmond Road  
Mobile, Alabama 36608

for

Sieve and Hydrometer Analysis

Organic Carbon-Carbonate Carbon Determination

Organic Carbon Determination

and

Ion Site Partitioning Stripping Procedure



# UNIVERSITY OF SOUTH ALABAMA

## SEDIMENTOLOGY LABORATORY

### SIEVE AND HYDROMETER ANALYSIS PROCEDURE

1. Air dry sample if possible; otherwise dry in oven at 110° F (maximum)
2. If consolidated, disaggregate sample using a rubber policeman (do not use a mortar and pestle as this will cause breakage of grains and alter the natural size properties of the sample).
3. Weigh out approximately 40 grams and record weight to nearest 0.01 g. Do not attempt to obtain a weight of *exactly* 40 grams as this will bias the sample.
4. Place the sample in a Mason Jar and add approximately 300 ml distilled (or deionized) water. Add 20 ml of a 10% sodium hexametaphosphate (by volume) solution. Stir and let stand for 6 hours (or overnight).
5. Transfer the sample to a soils stirrer and stir on *medium speed* for 5 minutes.
6. Pour the sample into a 1 liter hydrometer cylinder. Use a wash bottle to insure that all sample has been transferred into the hydrometer cylinder.
7. Bring the cylinder to a volume of approximately 800 - 900 ml with distilled (deionized) water. Let stand for 6 hours and check for flocculation. If flocculation is observed, add an additional 20 ml of the 10% sodium hexametaphosphate solution, stir, and let stand again for 6 hours\*.
8. If no flocculation is observed after 6 hours, the samples can be brought to a 1 liter volume and a normal hydrometer analysis can be performed. Readings are taken using a 152H ASTM hydrometer (following initial vigorous stirring of the sample) at the following intervals: 2, 5, 15, 60, 240, 720 and 1200 minutes. The temperature of the sample must also be recorded when each reading is taken to correct for the viscosity of water.
9. Following the 1200 minute reading, the sample is then washed through a 230 mesh (62.5 micron) or 270 mesh (53 micron) sieve. That retained on the sieve is washed onto a drying pan and oven dried. The oven-dried material is then subjected to a standard sieve analysis (see ASTM Method D 422-63) using either a whole phi or half phi interval.
10. Standard practice is to then calculate the measures of central tendency (mean diameter and median diameter) and dispersion (coefficient of sorting, skewness, and kurtosis) using either the methods of Krumbein and Pettijohn (1938), Inman (1952), Folk and Ward (1957).

\* **NOTE:** if flocculation is still taking place it has probably resulted from either: (1) the sample contains dissolved salt adhering to the grains or (2) excessive organics are present. If (1), the sample will have to be treated by dialysis; if (2) the sample should be pre-treated with 30% hydrogen peroxide to remove the organic component.

UNIVERSITY OF SOUTH ALABAMA GEOCHEMISTRY LABORATORY  
ORGANIC CARBON-CARBONATE CARBON DETERMINATION

Reagents:

1. Acid solution (6N HCl). Dilute HCl 1:1 with deionized water passed through organic-scrub filter.
2. Buffer solution (pH 10). Dissolve 67.5 grams of ammonium chloride in 200 ml deionized, organic-scrubbed water; add 570 ml reagent grade concentrated ammonium hydroxide, and dilute to 1 liter.
3. Potassium cyanide solution (2% solution). Dilute 10 grams in 500 ml of deionized, organic-scrubbed water.
4. Eriochrome Black-T indicator solution. Dissolve 0.2 grams of the indicator powder (Eastman Kodak, P6361) in 50 ml of analytical reagent grade methanol or triethanolamine containing 2 grams of hydroxylamine hydrochloride.
5. EDTA solution. Dissolve 4 grams of EDTA (disodium dihydrogen ethylenediamine tetraacetate) in one liter of deionized, organic-scrubbed water.

Standardize:

Standardize these reagents against U.S. Bureau of Standards Dolomitic Limestone 88B which contains a known amount of total soluble alkaline earths.

Determination of Carbonate Carbon

(Turekian, K.K., 1956, Rapid technique for determination of carbonate content of deep-sea cores: Am. Assoc. Petrol. Geol. Bull. 10:2507-2509)

Procedure

Sample Preparation:

1. Weigh 20 mg (0.020 g) of finely ground sediment and place in a 125 ml Erlenmeyer flask. Label flask with Sample ID and weight.
2. Add about 5 ml of acid solution and heat on a hot plate (in fume hood) until completely dry. Remove flask from heat and allow to cool.
3. Add approximately 1 ml of acid solution to flask to dissolve soluble material.
4. Dilute with 50 ml of deionized, organic-scrubbed water.
5. Add 5 ml of the buffer solution.

6. Add 2 ml of potassium cyanide and 10 drops of indicator. The sample should be some shade of purple (or possibly blue).

#### Titration

1. Record the volume of EDTA solution (to nearest 0.5 ml) in the burette prior to beginning titration.
2. Place a clean magnet in the flask and place flask on illuminated magnetic stirrer.
3. Titrate sample solution with EDTA. The end point occurs with a change in color from "wine red" to "true blue."

#### NOTE:

The color of the original sample solution is dependent upon the amount of soluble alkaline earths present in each sediment sample. For this reason, the color of the sample solution can be wine red (for a sample with abundant soluble alkaline earths), bluish-purple (for a sample with moderate amounts), or blue (for a sample with none, or trace amounts only). The end point of the titration is not always a rich blue, but may be light blue or even gray. Regardless, the end point will be easy to identify.

4. When the presumed end point is reached, note the burette volume and then add another drop (or more) to see if further color change occurs. If a change does occur, record the new volume.
5. Remove the magnet from the flask and wash with deionized, organic-scrubbed water; place in next sample to be analyzed.
6. When analysis is complete, dispose of solutions according to posted laboratory instructions.

#### Calculations:

The percent calcium carbonate is calculated by the following formula:

$$\% \text{CaCO}_3 = (\text{standardization constant}) \times (\text{titration volume}) / \text{Sample Wt} \times$$

\* sample weight in milligrams

$$\% \text{ Carbonate Carbon} = (\% \text{CaCO}_3) \times (0.12)$$

#### Discussion:

The standard solution is standardized in terms of millimoles of alkaline-earth per ml of solution. Stoichiometrically this must be equivalent to the millimoles of  $\text{CO}_3^{2-}$ . Hence, it is possible to derive the  $\text{CaCO}_3$  content. Two basic assumptions are used:

- 1- all of the soluble alkaline earths are present as carbonates and all carbonate is bound to the alkaline earths
- 2- no measureable alkaline earths bound to the silicate fraction are released with dilute HCl treatment.

## ION SITE PARTITIONING STRIPPING PROCEDURE

### PORE WATER PHASE

Homogenize approximately 30 grams of wet sample. Centrifuge at 6,000 RPM for 10 minutes. Vacuum filter supernatant through a 0.45  $\mu$ m membrane filter and preserve at 4° C for analysis.

### EXCHANGEABLE ION PHASE

Using sediment residue from pore water phase, add 100 ml of deoxygenated 1N ammonium acetate solution and agitate flasks for 1 hour using a wrist shaker. The solid to extractant ratio should be 1:5. Centrifuge at 6,000 RPM for 5 minutes and then vacuum filter the supernatant through a 0.45  $\mu$ m membrane filter. Preserve supernatant at 4° C for analysis.

### EASILY REDUCIBLE PHASE (Ions associated with disseminated $\text{MnO}_2$ compounds)

Using approximately 2 grams (dry weight equivalent) of sediment residue from exchangeable ion phase, add 100 ml of 0.1M hydroxylamine hydrochloride - 0.01M nitric acid solution. Solid to extractant ratio should be 1:50. Agitate sample for 30 minutes on a wrist shaker and then centrifuge at 6,000 RPM for 5 minutes. Filter supernatant through a 0.45  $\mu$ m membrane filter and preserve at 4° C for analysis.

### ORGANIC, SULFIDE, AND CARBONATE PHASE

Sediment remaining from easily reducible phase is digested in acidified 30% hydrogen peroxide in a 95° C water bath. Following this treatment, 100 ml of 1N ammonium acetate is added and the sample shaken on a wrist shaker for 1 hour. After shaking, the sample is centrifuged at 6,000 RPM for 5 minutes. The supernatant is poured off, filtered through a 0.45  $\mu$ m membrane filter and stored at 4° C for analysis.

### MODERATELY REDUCIBLE PHASE (Ions associated with iron oxides and hydroxides)

Remaining sample is treated with 100 ml of sodium citrate - sodium dithionate solution and shaken for 17 hours on a wrist shaker. The sample is then centrifuged at 6,000 RPM and the supernatant passed through a 0.45  $\mu$ m membrane filter. Store sample at 4° C until needed for analysis.

### RESIDUAL PHASE (ions coordinated in structural sites in clay mineral lattices)

0.5 grams of remaining sample (dry weight) is sequentially digested in concentrated nitric acid and then concentrated hydrofluoric acid. Digestion is carried out in a high pressure Parr Bomb in a microwave oven using a "ramped" heating procedure. The digested sample is evaporated to dryness and then brought to volume in a 1% nitric acid solution. The sample is stored at 4° C until analysis is performed.